JOURNAL of the AIR POLLUTION CONTROL ASSOCIATION

Founded 1907

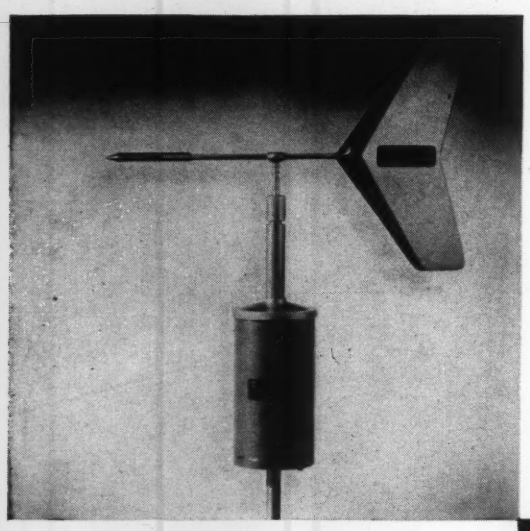
SCIENCE & TECHNOLOGY

Industrial Odor Control

(See Page 101)

FOR SYSTEM
APPLICATION

Wind Transmitters



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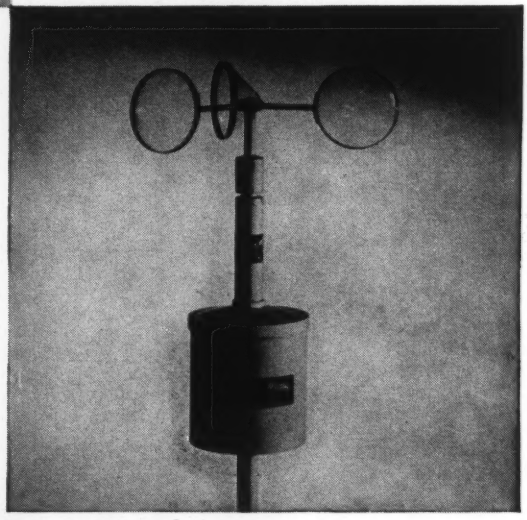
← WIND COMPONENT TRANSMITTERS with low threshold, providing sine and cosine vector resolution for wind-component determination. Also standard linear wind-direction transmitters in the same basic design.

→ WIND SPEED TRANSMITTERS based on dragfree light-beam chopper design, available in standard types providing one, two, four, and 100 pulses per revolution. Complete series housed in identical environment-proved package with triple-labyrinth dust-seals, selected and specially-processed low friction bearings. Extremely rapid transient response —guaranteed threshold three-quarters mile per hour.

Send for details on these standard units, or, if you have special problems, for recommendations on other instruments or special adaptations.



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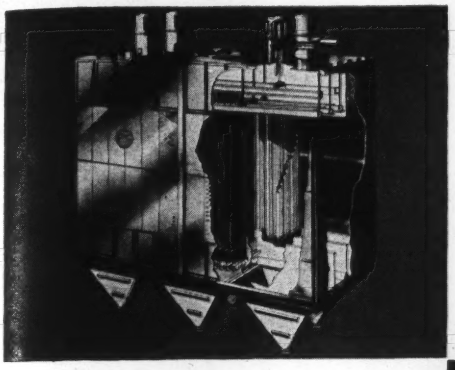
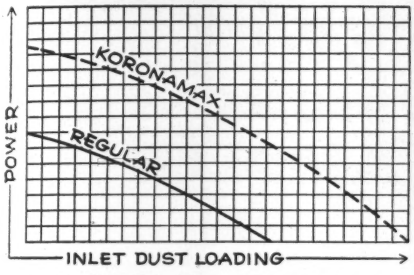
instruments for scientific meteorology

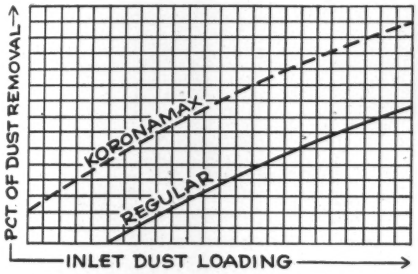


Another Koppers Exclusive in

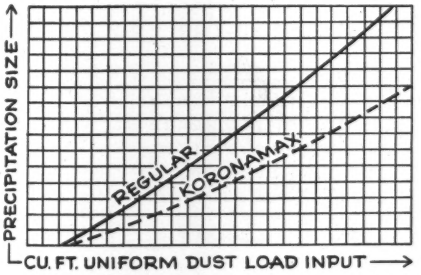
ELECTROSTATIC PRECIPITATION



INCREASED POWER—The evenly spaced discharge points of "Koronamax" Electrodes reduce the arc-over tendency and permit increasing power input.



HIGHER EFFICIENCY—Replacement of regular electrodes with "Koronamax" Electrodes allows higher power input — greatly increased efficiency.



SMALLER SIZE—In new installations desired efficiency may be obtained with smaller unit when "Koronamax" Electrodes are used.

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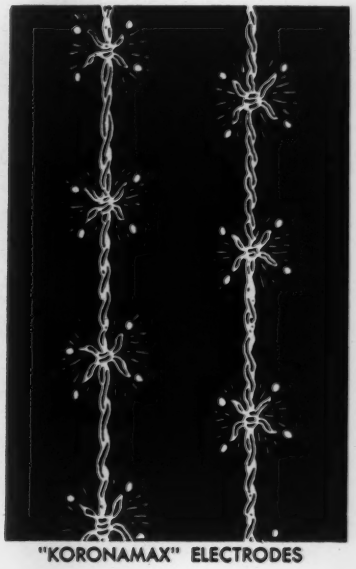

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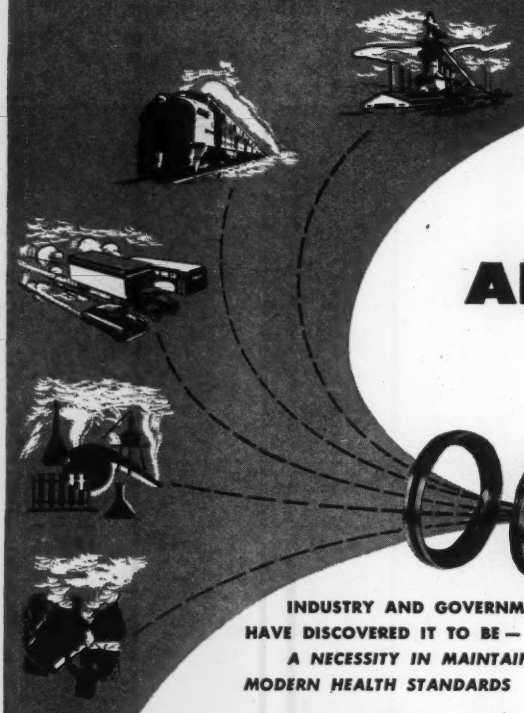

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HAVE DISCOVERED IT TO BE —
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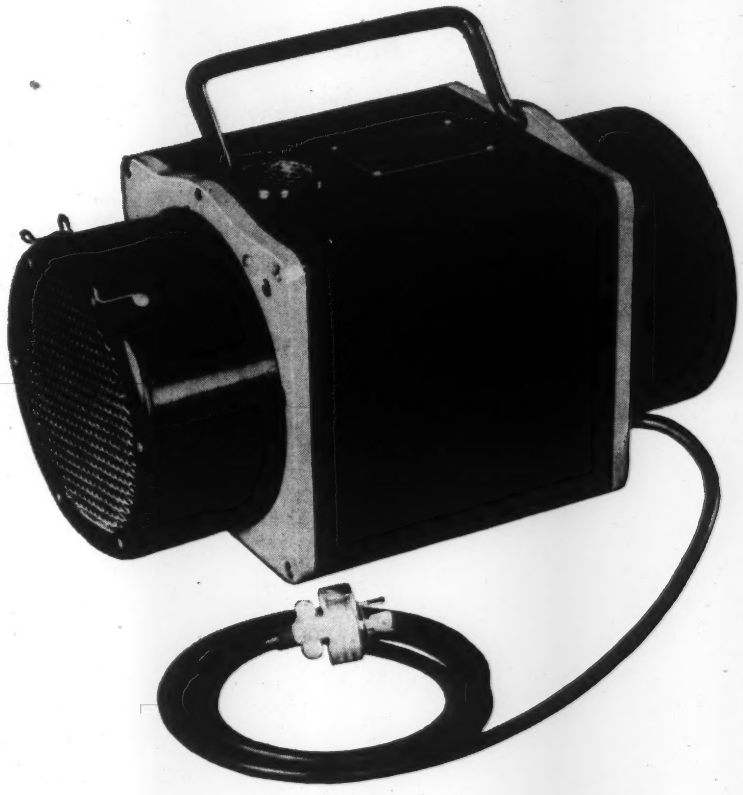

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Because accurate interpretation of data depends upon the knowledge of the volume of air drawn through the filter, this instrument is a vital contribution to industrial hygiene and air pollution personnel concerned with aerosol contaminants. The unit collects large samples on filters for weighing and analysis. It is easy to operate. It is compact (7¼" x 7¼" x 15") and weighs only 13½ pounds.

Complete information on operation, filters, and calibration is given in our bulletin. Write for a copy.

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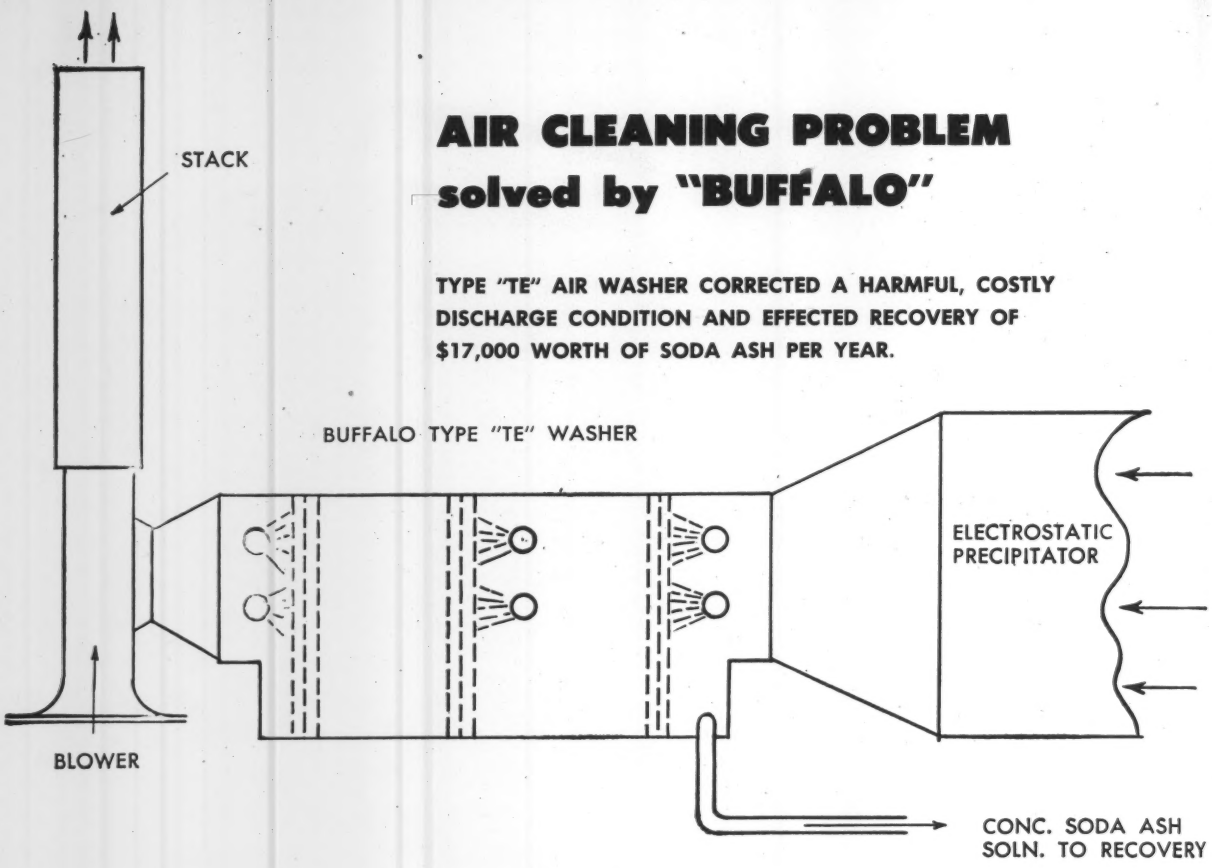
TYPE "TE" AIR WASHER CORRECTED A HARMFUL, COSTLY DISCHARGE CONDITION AND EFFECTED RECOVERY OF $17,000 WORTH OF SODA ASH PER YEAR.



PROBLEM

A paper firm was suffering poor community relations due to a soda ash discharge from its recovery plant. The ash, flaking off the collecting plates of its large electro-static precipitator, was damaging auto finishes.

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Installation of a "Buffalo" 84,000 cfm Type "TE" Washer as shown. Washer is all-stainless construction, with two wet scrubbing stages and one eliminator stage. Scrubbing water was recirculated thru spray nozzles at 20 psi until soda ash became concentrated enough for efficient collection.

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Whatever the contaminant, whatever the removal problem, chances are excellent that a "Buffalo" Unit is controlling a similar condition in your industry to complete satisfaction. Write for details today — take advantage of our long experience in industrial air cleaning.

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INDUCED DRAFT	EXHAUSTING	FORCED DRAFT
COOLING	HEATING	PRESSURE BLOWING

FOUNDED 1907

JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION

(Formerly "Air Repair")

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Devoted To
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The Editor welcomes writers interested in air pollution problems and encourages them to use the pages of this journal for the expression of their opinions. But neither he nor the Association assumes responsibility for the validity of the opinions expressed herein.

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In Charlotte, North Carolina

A. I. S. I. SAMPLER readings reveal year-to-year improvements in AIR POLLUTION CONTROL

By making a graph of A.I.S.I. Sampler readings in Coh Units, Charles S. Frost, Director of the Charlotte, N. C. Department of Air Pollution Control, maintains an hour-by-hour, day-to-day, and year-to-year record of air pollution conditions in Charlotte.

Results of any air pollution regulations put into effect can be determined almost immediately by reading the A.I.S.I. Sampler recordings.

Charlotte, which is constantly improving conditions in cleaner air, is one of many municipalities throughout the country who are maintaining air pollution records based on the readings of the A.I.S.I. Sampler.

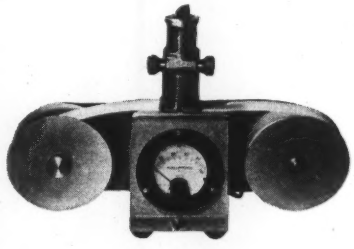
The low cost of the A.I.S.I. Sampler makes it feasible to locate a large number of them for complete coverage of a geographical area; and its quiet operation overcomes any objections to its location in or near individual residences.

Research Appliance Company manufactures another sampler, the A.I.S.I. Hydrogen Sulphide Sampler, which measures the amount of hydrogen sulphide in the air. It can indicate H_2S concentration as low as one part per billion parts of air.

It operates on the same principle as the Air Sampler, but is fitted with an air filter to remove suspended solids; and the tape assembly is enclosed to prevent blackening of the tape, outside the sample spot.

TO ANALYZE THE SPOTS, Research Appliance Company manufactures a Spot Evaluator with which spots are evaluated by measurement of light transmission.

Write for descriptive bulletins that give complete construction and performance details of both the samplers and the Spot Evaluator.



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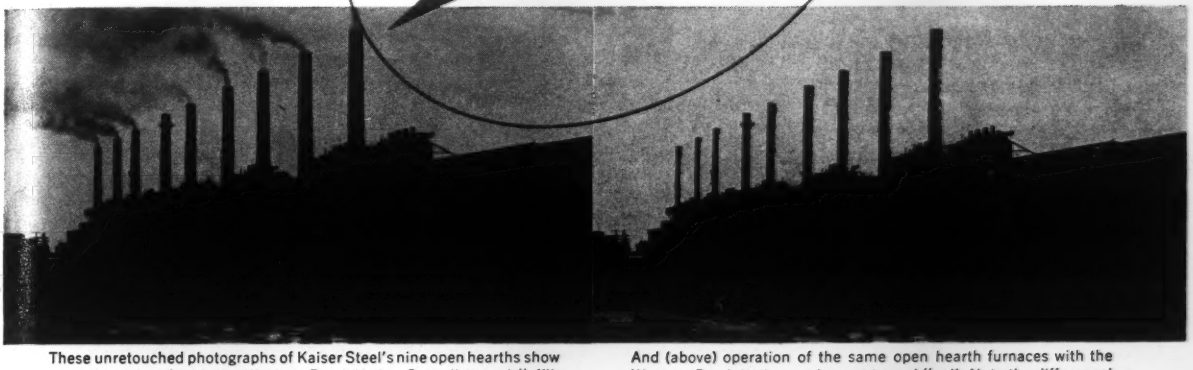
MODERN SMOKE CONTROL PROGRAM



These unretouched photographs of Kaiser Steel's nine open hearths show operation (above) with the Western Precipitation Cottrell turned "off".

And (above) operation of the same open hearth furnaces with the Western Precipitation equipment turned "on". Note the difference!

As part of one of the most progressive dust and fume control programs of any steel mill in the United States, Kaiser Steel Company recently placed "on stream" the last of nine Western Precipitation Cottrell Precipitators to control dust and fume from its nine open hearth furnaces. This installation is particularly interesting for several reasons . . .

1. Culmination of a long period of development work by Kaiser Steel and Western Precipitation engineers, this installation marks the first application of Cottrell Precipitators to the unique problems of dust and fume control on hot-metal open hearth furnaces.

2. To handle efficiently the wide fluctuations characteristic of open hearth operations, the units are equipped with Western Precipitation's new "Transistomatic" Controls to insure continuous and automatic voltage adjustment to varying load requirements.

3. These nine Western Precipitation units are ONLY PART of the complete line-up of Western Precipitation equipment installed in this plant. Other Western Precipitation units include BLAST FURNACE PRECIPITATORS for cleaning blast furnace gases . . . DETARRING PRECIPITATORS for cleaning coke oven gases . . . and SPECIALIZED DUST VALVES for simplifying collection operations.

Kaiser Steel states "The very nature of steel production involves furnace heating of large quantities of iron ore, coal, limestone, and other minerals each year. There is no escaping the fact that this activity results in smoke and dust. The Western Precipitation installation . . . represents the result of seven years of research, experimentation, engineering, and construction effort. The equipment does an amazing job."

Naturally, we of Western Precipitation are proud to have played an important role in bringing modern dust and fume control to yet another segment of industry—open hearth steel operations. Our more than a half-century of experience in Cottrell Electrical Precipitator applications throughout the world is at your service. May we study your particular requirements in air pollution control and make helpful recommendations?

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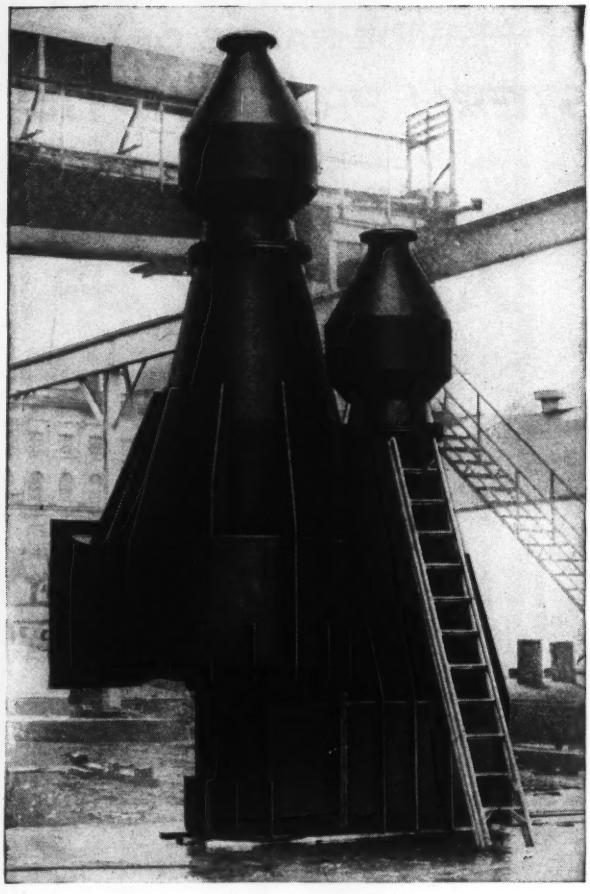

Exploring new frontiers!

BUELL CYCLONES

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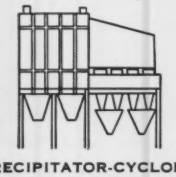
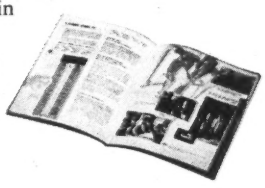


PRECIPITATOR-CYCLONE COMBINATIONS

But these aren't satellite launchers, though they're specially designed for high temperature operation: they're Buell extra-efficient cyclone dust collectors . . . and the new frontiers they're exploring are in industry. Everywhere in American industry, from cement mills to refineries, from chemical plants to power generating stations, Buell collectors set new records in percentage of dust removed, low maintenance, and improved plant operation. Even in the age-old field of fly ash collection, Buell extra efficiency pays off. Only *Buell* cyclones have the unique Shave-off port that traps small fines in the double eddy currents. And Buell large-diameter design eliminates bridging, clogging, or plugging. *All three* Buell Systems are illustrated and described in "The Collection and Recovery of Industrial Dusts". Write for a copy to Dept. 51-H, Buell Engineering Company, Inc., 123 William St., New York 38, N. Y.



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Industrial Odor Control*

JOHN VON BERGEN
Airkem, Inc.
New York City

Odors and fumes are the natural by-product of many chemical manufacturing processes.

Up until a few years ago, odors were considered something inevitably present around many chemical plants. But recently a number of methods have been developed for controlling or eliminating industrial odors.

Most odors emanating from chemical plants are not physically dangerous. But they have proved to be psychologically dangerous. The fact that they do not cause organic disease is a difficult point to prove — particularly when the surrounding community, submerged in a disagreeable odor, has been aroused by uninformed rumors and misleading information.

The new methods of odor control have accomplished much in a short time for the improvement of community relations and plant employee morale. These factors, together with concern over depressed property values due to odor, and the general discomfort of odorous areas, have all combined in opening the doors to an intelligent and logical approach towards this problem.

Industrial odors are now recognized as a very definite part of the over-all air pollution picture. Chemical engineers concerned with the design, supervision or administration of chemical plants should become familiar with the latest methods and techniques available for controlling industrial odors.

Some odors are conveyed on liquid and solid particles. Filters, electrical precipitators, sonic flocculators, cyclone scrubbers are available for removing these particles. (See *Chem. Eng.* Oct. 1953.) Most odors occur in the gaseous phase and we will restrict our discussion to this type of problem.

FIRST STEP: ODOR SURVEY

A survey of chief public officials responsible for the control of air pollution in 67 major industrial cities was conducted in 1955.[1] Tabulation of answers to the following specific questions was made:

Q. Do you receive many complaints about odors either separate from or accompanying other forms of air pollution?

A. Many complaints were reported by 78% of the respondents. More than half of these judged that the number of complaints were increasing.

Q. Do you feel there is increasing public interest in odor problems in your community?

A. Yes	68%
No	20%
No answer	12%

Q. Would you please indicate the sources of odors in your community at this time or in the past? (In order of frequency of mention, here are the sources of odors. The figures refer to the % of questionnaires in which the source was cited.)

A. Chemicals	62%
Vehicles	52%
Paint and varnish	49%
Food processing	47%
Domestic (homes, *etc.*)	45%
Rendering plants	43%
Plastics	33%
Oil refineries	31%
Coke works	31%
Rubber	27%
Steel	25%
Insulation	21%
Fish	21%
Gas works	19%
Pharmaceutical	19%
Soap and detergents	17%
Breweries	15%

These summaries are significant. Our industrial growth has resulted in the production of great quantities of products which were unknown at the beginning of the 19th century. Our automobiles alone pour 7 million tons of exhaust gases into the atmosphere daily. The chemical industry has experienced a seven-fold increase in sales over the past 30 years, and this growth is continuing at a phenomenal rate.

In spite of many other sources of air pollution, the fact remains that many individuals continue to blame chemicals in general for increased air pollution problems. It is inevitable that control agencies will increase the pressure for odorous air pollution abatement as time goes on.

Chemical engineers stand directly in the path of this pressure buildup and the chemical industry has many serious odor problems for which it needs answers.

Remove Odor at Source?

It is possible, of course, to control odors by eliminating or reducing their source. This may involve rearranging or subdividing the molecules of aldehydes, diamines such as putrescine and cadaverine, ethylamines, indoles including skatole, thiomides, hydrogen sulfide, ammonium sulfide, organic acids, phenols, cresols, isocyanides or carbylamines, ketones, mercaptans, mercaptides methylamines, thiocyanates and many other compounds discharged by chemical process industries.

Specific treatments that can be applied may fall in the classical chemical reactions: neutralization, acidification, alkalization, oxidation, reduction, hydrolysis, polymerization, *etc.* Improvements in process methods, equipment and housekeeping can reduce the volume of exhausts.

If the gaseous wastes of an industrial process are known or can be pre-

*Reprinted from *Chemical Engineering*, August 1957. Copyright 1957, McGraw-Hill Publishing Co., Inc., 330 West 42nd Street, New York 36, New York.

Effective Methods for Controlling Industrial Odors

- **Combustion**
- **Absorption**
- **Adsorption**
- **Odor Masking**
- **Odor Counteraction**

Most Common Sources of Odor

Fertilizer manufacturers Fish wastes. Spent acids.	Trimethylamines.
Canners and food producers Effluents and dumps.	Mercaptans, reduced sulfur compounds.
Tanneries Effluents and dumps.	Products of nitrogen compound decomposition.
Pharmaceutical plants, breweries Fermentation wastes.	Reduced sulfur compounds, caproic acids.
Petroleum refining Effluents, waste gases.	Amines, reduced sulfur compounds.
Municipalities Dumps, lagoons, settling ponds.	Mercaptans, H_2S, ammonia.
Chemical manufacturers Resins, adhesives, rubber, paints, varnish coatings, fats, oils, etc.	Product of nitrogen compound decomposition.
Textile and paper Dumps, settling ponds, lagoons.	Phenolics, sulfur compounds, formaldehyde, solvents.
	Urea, starch decomposition products.

dicted with some assurance, their possible destruction may be ascertained by a study of the literature.

Actually, in most cases, analysis of chemical constitution of a complex odor is a very difficult job. Almost as troublesome as composition, is the possibility of multiple odor sources. Also, a change in process is seldom practical or economical.

To avoid neighborhood complaints and generally bad public relations the chemical engineer should explore an ounce of prevention. This ounce of prevention can take the form of a careful study on plant odor offense possibilities in the surrounding neighborhood area.

How to Appraise Odor

The atmosphere surrounding a plant has great capacity for dispersing odorous effluents. Favorable influences are stack height, gas velocity and gas temperature. Adverse influences are aerodynamic, terrain and meteorologic.

Under favorable weather conditions, odors from a plant will rise gradually as they flow downwind. Contaminants will disperse until only a negligible concentration prevails in the atmosphere. Under these conditions and conditions of actual vertical dispersion, odors do not ordinarily become an annoyance in the complaining area.

There are many natural influences, however, which arise to disturb this orderly dispersion. Wind flowing past a plant generates turbulence in the wake of stacks and buildings. Turbulent masses of odor above and behind the buildings are brought down to the ground in a spreading area. This is termed downwash. Under these circumstances, concentrations of odors may be very high in an area close to the plant.

If odor escapes the downwash situation at the plant, it may flow downwind and come under the adverse influence of terrain. Hills or valleys and bays and pockets may set up currents which entrap the odors. Thermal influence in the atmosphere plays a large part in the over-all air movement. Under conditions of air inversion, large quantities of odors are brought to the ground over a large area and sometimes held for hours.

Behavior pattern, dispersion and diffusion of plant odors is important to valid odor survey work. Sherlock and Lesher[2] describe in detail conditions of waste gas flow with light wind and strong wind under neutral or stable atmosphere. In addition, they describe the action of the gas plume under conditions of idealized diffusion, thermal looping in an unstable atmosphere, gustiness looping, and meandering of gas plumes. This work is helpful in understanding the basic problems of odor dispersion.

Set Up an Odor Jury

In appraisal of odor dispersion an odor jury is important. Although the nose is a delicate instrument the physiological and psychological reactions many times distort the perceptive impression.

Moncrieff[3] has mentioned these basic facts regarding human olfactions:

(1) All normal people can smell.

(2) People suffering from brain lesions, injured olfactory nerves or obstructed nasal passages may be anosmic (incapable of perceiving odors).

(3) Cases of preferential anosmis or ability to sense certain smells and not others, do occur.

(4) Characteristic of an odor, as well as the intensity, may change on dilution.

(5) Sense of smell is rapidly fatigued.

The problem of measuring psychological acceptability is a complicated one. A fair number of persons, for long periods of time, continuously or continually are beset by odors without the presence of the material ordinarily causing such odors. Cases of illness or irritation make people perceive or imagine odors that do not exist.

Although it has been stated that one of the most dependable methods for ascertaining odor appraisals in air pollution work is a population survey, this does not mean selecting a few residents who have made complaints in the past. Some residents have complained of odors three months after a plant has been shut down.

In spite of this, all normal people can perceive odors, and the most important method of gas analysis ever employed is the sense of smell. Smelling has some limitations, mostly quantitative, but has many advantages over other means of analyses. Sampling is automatic. Analysis is made and the results reported almost instantly. And the apparatus (the nose) is nearly always in a position to obtain the sample of greatest immediate interest. No other present method of analysis is capable of distinguishing between, and correctly re-

porting, so large a variety of chemical substances by a single operation.

Some Principles of Odor

A great deal of odor exploration has been extended to the organic series embracing aromatic hydrocarbons, alcohols, phenols, ethers, organic acids, aldehydes, amines, ketones, ketals, halogen compounds, nitrogen compounds, sulfur compounds, paraffins, esters, and others. Such exploration involves saturation and unsaturation, open chains, closed chains, straight chains and branched chains, isomerism, odor carriers, and odor extenders.

The outstanding facts established indicate that no single pattern of chemical structure serves to maintain even a trend of properties. Complexity of odor research, and for that reason the value of using the experience of the odor chemist, is indicated by a very few of the hundreds of principles that have been advanced by odor researchers.

The few principles listed below are only an indication of the complex problems involved.[7]

- Compounds of different constitutions may have similar odors (camphor, silicononyl alcohol, durene).
- Compounds of very similar constitution may have different odors. If, however, the constitutional differences are slight, odor differences are generally correspondingly slight.
- Polymerisation reduces or destroys odor whether in elements (red phosphorus) or in compounds (glycols).
- Unsaturation enhances odor but does not initiate it (paraffins are odorous).
- In the paraffins, straight and branched-chain isomers have similar odors.
- In a homologous series the odor will rise to a maximum as we ascend the series and will then fall off owing to decreased volatility.
- Unsaturation often introduces an irritant note to the odor particularly if close to a polar group (aliphatic aldehydes and acids).
- A tertiary carbon atom will frequently induce a camphoraceous odor.
- Osmophoric influence of the phenyl group is strong. It overcomes that of alkyl-ether groups and also of the amino group.

Rating Systems Are Helpful

To obtain valid surveys it is important to have at least seven persons included in an odor jury. Observers are not necessarily required to demonstrate unusual olfactory acuteness or discrimination to qualify for a panel. On the other hand, the observers should try to be objective in their opinions. Technically trained laboratory personnel are excellent for this reason.

The jury requires a list of descriptive and easily identifiable terms for a uniform description of odor. Most lay people attempting to describe an odor grope for words, as if they were talking a foreign language. Odor memories are short and are susceptible to outside influences. If one has been told there is an odor of dead fish from a certain plant because of failure, every odor from that plant could smell like dead fish to the untrained observer.

A definite route for odor observations should be established based on sources of odor complaints in the past, wind directions and topographical situations. Each observer should be equipped with a report form on which he can indicate wind direction and velocity, location of observation, time, suspected source, technical description, strength, and description of odor sensation.

A rather simple scale for odor component intensity follows:

0—no odor, or no odor of the designated component.
1—threshold level of the component.
2—definite odor of the component.
3—strong odor of the component.
4—overpowering odor of the component.

This scale is readily memorized and does not require frequent reference to a descriptive intensity scale. It is also convenient for half-scores when the observer is in doubt as to intensity level. For comparative purposes, most observation runs should be at approximately the same time of the day. Usually, the best time for observation is in the evening when air inversion occurs and most residents are at home. The evaluations may continue until midnight, and some observations should be made in the early morning hours.

Although it is not advisable to make surveys of the opinions of residents, complaints initiated by residents become an important part of the survey, assuming the complaint is valid. All complaints should be listed as to date, exact location, length of residence, description of odors as can be best obtained, the number of times the particular odor was noticed over a period of time, and the time of day the odor was noticed. All of this material can be collected and shown graphically in an excellent method by Gruber.[4]

A careful survey, coupled with a report on residential complaints, is the basis for determining the most practical method of odor abatement.

METHODS OF ODOR CONTROL

Methods now commercially available for the control of odors from exhaust stacks may be divided into five general classifications: combustion, absorption, adsorption, odor masking, and odor counteraction.

It might be pointed out here that the dilution and dispersion technique, where odor-containing gases are put through a high stack, does decrease odor intensity. But this alone is not a generally recommended practice for odor control or elimination. It depends too much on wind and atmospheric conditions, which cannot be controlled or predicated.

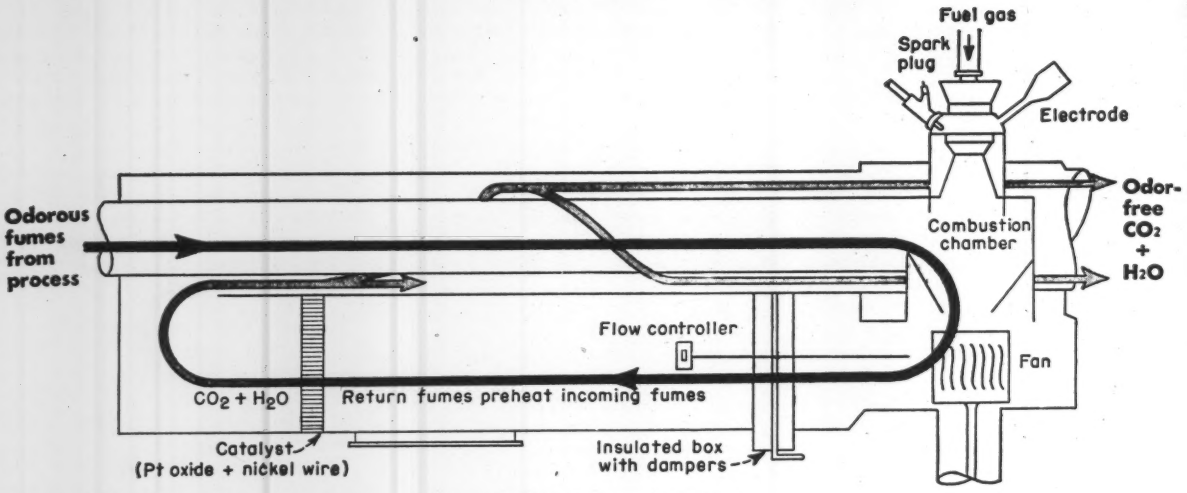
COMBUSTION METHODS

Fire is one of the oldest known methods of odor destruction. It is not a method of odor control, however, unless it is complete combustion. Incomplete burning of nitrogenous and sulfurous organic material with the resultant pungent oxides of nitrogen and sulfur is not the ideal conclusion to an odor destruction process.

Partial combustion may be worse than no combustion — evidenced by incinerators or the incomplete combustion in diesel and internal combustion engines which yield the irritating and sickening aldehydes, with formaldehyde as the principal ingredient in this group.

From a theoretical standpoint, if complete oxidation of odors in the air can be obtained, deodorization is obtained because the final products are odorless (H_2O, CO_2) or have a higher odor threshold than the products consumed. For example:

Butanol — Mild odor
↓ O_2
Butyraldehyde — Bad odor
↓ O_2
Butyric acid — Very bad odor
↓ O_2
$CO_2 + H_2O$ — Odorless



Courtesy Catalytic Combustion Corporation

Fig. 1. Catalytic fume combustion unit.

Considerable progress has been made in an attempt to reach complete deodorization by use of catalytic burners, particularly in eliminating odors from fats, oils and fatty acid processes. The only limitation of a catalytic burner is that the combustible substance introduced into the burner must be in the vapor phase or must be vaporizable at a reasonable temperature. Noncombustible inorganic solvents are not affected by a catalyst and should be absent from the air stream.

As to complete oxidation, it must yield innocuous products in order to serve the purpose of odorous air pollution control. In the compounds of carbon, hydrogen and oxygen, which cover a wide field, this is true. In the case of hydrogen sulphide or organic compounds containing sulphur, catalytic combustion operating at temperatures below 675°F. or above 1,250°F. will convert sulphur to sulphur dioxide — less offensive and less dangerous than many of the original substances as long as the dispersal level is well below the maximum permissible level in the neighborhood.[5]

General rules for organic compounds containing nitrogen are difficult. The effluent may contain free nitrogen or its oxides depending on the conditions of operation. Reduction of nitrogen oxides will, of course, release free nitrogen.

Catalysts Lower Temperature

Use of catalysts to aid combustion is illustrated by the design of platinum alloy activated alumina coating on porcelain rods or platinum alloy coating on nichrome wire.

Odorous air, passed through a catalytic device, may be oxidized at temperatures 500-800°F. lower than required by uncatalyzed incineration. A major contribution offered by catalytic combustion is the considerable lowering of the firing temperature, with resultant saving of energy for heating air, and capital equipment costs for heating capacity.

Some combustion processes may operate without an outside energy source, except for that required to reach the firing temperature. Or with smaller fuel requirements, where such operation would normally have been economically unfeasible in uncatalyzed incineration (Fig. 1).

Temperature for effective combustion deodorization depends to a great degree on the chemical nature of the vapor to be oxidized and on concentration in the inlet stream. Self-sustaining catalytic combustion is attainable normally in concentration ranges of 15-20% of the lower explosive limit. When the concentration falls below 5% of the lower explosive limit, operation of catalytic combustion becomes more costly because of the decreased heat content and increased firing temperature (see Table I).

In order to achieve maximum benefits, engineering design under the guidance of catalytic reaction experts, is very important in the application of catalytic processes. Each process must be studied in relation to stream temperature; variability of

TABLE I*

HEAT CONTENT OF MAJOR OXIDIZABLE POLLUTANTS IN AIR

	Basis	Heat Content of Air Mixture, Btu./cu. ft.	Temp. Rise, F.[a]
Pollens, bacteria, dust, fibers, smokes			
200 mg./cu. m.	8,000 Btu./dry lb.	0.099	5.5
Carbon monoxide			
1,000 ppm.	321.8 Btu./cu. ft.	0.322	18
3.15 vol. %, ¼ LFL[b]	321.8 Btu./cu. ft.	10.16	565
Hexane (normal)			
100 ppm.	4,412 Btu./cu. ft.	0.441	25.5
0.315 vol. % ¼ LFL[b]	4,412 Btu./cu. ft.	13.90	770
0.63 vol. %, ½ LFL[b]	4,412 Btu./cu. ft.	27.80	1,540
Hydrogen sulfide			
1,000 ppm.	596 Btu./cu. ft.	0.596	33
1.08 vol. %, ¼ LFL[b]	596 Btu./cu. ft.	6.44	357

*W. R. Calvert, Catalysts at Work Eliminating Air Pollutants. *Proc. 49th APCA Annual Meeting.* Buffalo, N. Y. May 20-4, 1956.
(a) 100% catalytic reaction (no heat loss).
(b) Lower flammability limit.

the concentration of oxidizables; volume and space rate of the stream through the catalyst; oxygen content of the stream; attrition and the effects of the loading of the catalyst with inorganic matter.

As with any other process used in air pollution control, there are cost considerations which must be weighed against benefits achieved.

The most readily accepted catalytic processes are those which yield usable heat with the possibility of writing off the investment with heat savings. Heat transfer may be used to bring the stream of waste effluents to a satisfactory firing temperature level. After once starting the catalytic process, product heat can be recirculated or used to heat the incoming stream. Where fuel must be used to heat a stream to a level necessary for sustaining the catalytic reaction, limiting cost becomes the cost of heating the entering stream less the value of heat leaving the catalytic process.

Variability and concentration of oxidizable material must be controlled in the catalytic process. Since the process depends on concentration level, upper and lower limits must be accommodated.

A concentration too low requires that the stream be preheated; a high concentration requires dilution. Where the limiting concentrations are of brief (a few minutes) duration, the heat retaining capacity of the porcelain supported catalyst automatically adjusts to accommodate the variation. Oxygen content of the stream need only be sufficiently in excess of the stoichiometric requirements to assure adequate distribution of oxygen to the catalyst.

Prolong Catalyst Life

Particulates of inorganic materials may not be a problem when velocities are low. Where the inorganic particulates have an abrasive or attrition effect upon the catalyst, the catalyst life is shortened. Where the inorganic particulates fuse readily or are in extremely high quantity, then the catalyst might become heavily loaded with this material and the catalyst life consequently shortened.

Loss of catalyst activity, which determines catalyst life and hence equipment maintenance cost, is related to three major factors:

- Presence of catalyst poisons (such as metallic or organometallic vapors) in the odorous air.
- Obstruction of the catalyst surface either by deposit of carbonaceous material by incomplete combustion of some contaminant or by mechanical adherence of particulate material.
- Mechanical loss of the catalyst by abrasion.

Specific catalytic poisons are vapors of pure metal, such as mercury, arsenic, zinc, lead, etc. These quickly stop catalytic action by permanently depositing on the active catalyst. Occurrence of high concentration of these substances is relatively rare in air pollution control problems.

For air free from particles and metal containing vapors, a long catalyst life may be realized. Some installations are reported to have given over 23,000 hr. of service without catalyst regeneration.[6]

Recovery of Heat Values

A pilot run, before installing full-scale equipment should be made, unless it can be definitely ascertained by other means that serious attrition or replacement factors are not involved.

As shown in the table, cleanup of low concentrations of combustibles will require additional energy. In terms of heat, energy recovery will be negligible considering the cost. Benefits and advantages will depend on better public relations and the avoidance of nuisance complaints in the surrounding residential area. Since air dilution of stack exhausts has long been used to avoid neighborhood complaints, it is possible that reconsideration and redesign of ventilation equipment to include employment of catalytic oxidation rather than air dilution can result in:

- Savings in heating fuel and air conditioning costs.
- A supply of heat from the catalytic oxidation, which can further reduce heating costs in addition to the primary objective of the elimination of odorous organic air pollutants.

A great deal of heat value can be recovered for high concentrations of combustibles which are safely below the lower flammability limits.

Steps to Follow in Combustion

An approach to removal of odors by catalytic combustion would involve the following steps:

- An analysis of stack gases and other exhausts to determine characteristics and quantity of odorous elements.
- A determination of those elements oxidizable in air and the heat

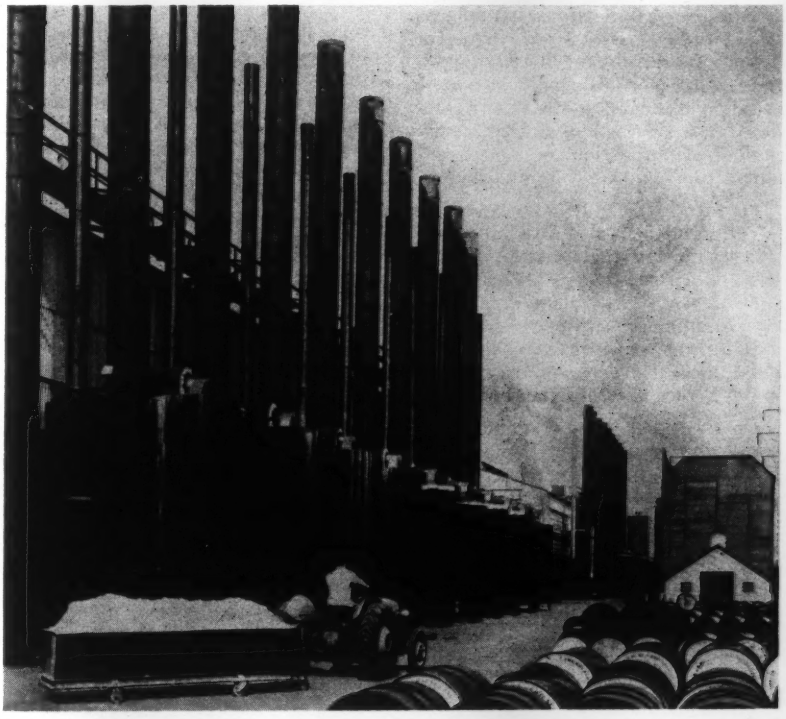


Fig. 2. Catalytic burners (nat. gas) eliminate odor at Reichold.

content per cu. ft., based on concentration.

• Estimates from a competent manufacturer of catalytic burners on the cost of installation, life expectancy of the unit, maintenance and efficiency in heat recovery and exchange.

• Preparation of cost analysis on the basis of calculated costs of operation, including investment vs. usable energy returns. Comparison of this method with the appraisal costs of other methods of odor removal, taking into consideration advantages and disadvantages of each method of operation which might affect your situation.

• If the catalytic combustion method appears to be the best solution, arrange for pilot-plant installation and ascertain the reliability of all estimates involved, in addition to observing the pilot burner exhaust for odorous content.

ABSORPTION METHODS

Where odorous vapors are soluble or emulsifiable in a liquid, with or without chemical reaction, absorption methods may be suitable for odor control.

Absorption is a word not without its confusing implications. It applies to a more or less uniform penetration of the absorbent by gas molecules and is not a concept restricted to liquid absorbents. In this discussion however, we will limit the discussion of absorption to the conventional process using liquid absorbents.

The fundamental forces of interphase diffusion that govern the absorption process are fairly well known. Equilibrium data, determination of number of stages, diameter, limiting velocity, are all covered in standard texts such as Perry, Sherwood, Brown or Badger and McCabe.

On the other hand specific, exact knowledge in the field is not comprehensive. One of the most troublesome applications is the removal of extremely small quantities of air contaminants that create odor nuisance. According to one concept, if a gas is highly soluble in liquid, then its diffusion in the liquid from the surface is relatively easy. This would indicate that resistance to absorption may be minimized by spraying the liquid through the gas, causing good turbulence on the gaseous side of the interface (around the outside of the droplets). For example, ammonia, highly soluble in water, is readily absorbed by spraying water through a chamber containing ammonia gas.

On the other hand for relatively insoluble gases (many odorous organic compounds if water is a solvent) the reverse would be true. Resistance of the liquid film at the interface between liquid and gas controls rate of absorption. To minimize resistance, it is usually recommended that the gas be bubbled through the liquid to obtain good turbulence in the liquid phase and facilitate gas absorption. For this reason spray washers or scrubbers have considerable difficulty in absorbing low concentrations of some gases.[7]

Commercially Available Equipment

Hundreds of methods have been devised to maintain air-liquid dispersal contact.

Increase in contact time or in the number of separate times the air encounters the spray zone greatly assists the absorption of vapor but performs an operation of diminishing utility. Methods used vary from the simple vertical spray towers in single or multiple stages; the cascade vertical tower; towers packed with partition rings, Raschig rings, spiral rings, Berl saddles, hollow balls, helical packers, hexahelix blocks, double spiral cyclohelix blocks, prismic packings; centrifugal or cyclone scrubbers; bubble and sieve trays, etc. An efficient scrubber (Fig. 3) uses a perforated sheet designed with a layer of impingement baffles above the sheet. Gas stream enters the liquid phase through the sheet and impinges against the baffle.

Height of an absorption tower increases its efficiency, while cross-section determines air capacity.

Liquids Other Than Water

In all types of air washers it is possible to modify the solvent. Neutralization of acidic odorents with sodium carbonate, dimethylamine, ethanolamines or oxidation with permanganate, chlorine, chlorine dioxide, ozone, is often effective.

However, liquid other than water may require expensive corrosion-resistant materials and possibly neutralization or stabilization of the waste water before discharged to the sewer. Discharge to a sewage system may answer the need for further treatment once the offensive odors have been collected and condensed in the wash water.

On the other hand the possibility that dissolved gases may later escape into the air and create an odor nuisance at open manholes or at the sewage plant itself should not be overlooked. Care must be taken that waste scrubbing solutions do not meet other solutions which will react and release the odor creating compounds to the atmosphere.

Also, remember when physical solution, without chemical reaction is involved in absorption methods, partial pressure of the odorous gas in equilibrium with the solution of such gas is a limiting factor. For all practical purposes deodorization by physical absorption is never a process which removes all odors.[6]

In most cases use of washing equipment is suitable for the removal of particulate material (although not as effective as electrostatic precipitators).

Steps to Follow in Absorption

Chemical engineers should take the following steps in considering washing, condensing, or scrubbing methods.

• Devise a laboratory scrubber and analyze the chemicals discharged into the waste water. Calculate the total chemical sewage effluent from any plant operation, including the exhaust stack wash per day or month.

• Prepare samples of the chemical sewage discharge and take them to the local sewage plant operator or state stream pollution officials if the discharge is into a river or stream. If the discharge is acceptable to local or state officials, get assurance (in writing if possible) that the discharge can be made during the reasonable lifetime of the proposed equipment. Many equipment manufacturers will supply pilot or laboratory equipment which duplicate the essentials of their designed equipment. Run a careful check on costs of operation, corrosion conditions, auxiliary pumping equipment, air handling capacity and required auxiliary equipment for supplying exhaust movement.

• The odor evaluation of a washed exhaust is difficult to appraise in a laboratory or plant area due to the presence of plant odors. For this

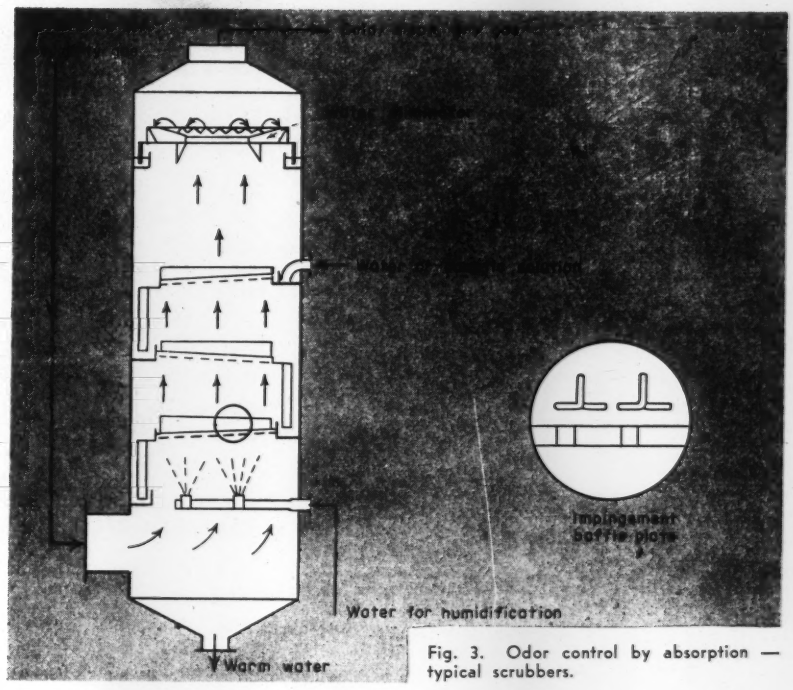


Fig. 3. Odor control by absorption — typical scrubbers.

Courtesy Peabody Engineering Corporation

reason final tests should be made in an odor-free room and by odor observers not conditioned to normal plant odors.

• If satisfactory results are obtained, compare an investment and operating appraisal with other methods of odor removal.

ADSORPTION METHODS

Adsorption is the phenomena of surface attractions universal with all substances. In theory it is agreed that adsorbed molecules do not penetrate the atomic or molecular construction of the adsorbent.

In adsorption there is interaction between the solid and gas. The bond may be broken by moderate elevation of temperature to drive off the chemically unaltered absorbate. This is physical adsorption rather than chemical adsorption (this discussion does not include capillary attraction).

Control of atmospheric odors by adsorption methods is for all practical purposes limited to the use of activated carbon as adsorbent. Metallic oxide, siliceous and active earth type adsorbents are electrically polar and have strong attraction for water, which is highly polar. Polar adsorbents retain water in preference to most other vapors and therefore are incapable of adsorbing non-polar or weakly polar gases (most organic vapors) selectivity from a moist atmosphere.

Activated carbon is electrically non-polar and consequently capable of preferential adsorption of organic material. Previously adsorbed moisture will be displaced from the carbon surface as organic acids and vapors are adsorbed.[6]

An advantage of using activated carbon is it adsorbs all types of odors under almost any condition. It can be used without making a careful analysis of odor content. Properties of gases and vapors and their retentivity by activated carbon are available.[8]

Equipment selection generally depends on requirements for total capacity, allowable pressure drop and space requirements. Over-all adsorption efficiency of activated carbon is practically 100% for vapors having a high retentivity value and remains so until the amount of material adsorbed is about two-thirds of the retentivity figure independent of moisture. Care must be used in replacing the activated carbon filters prior to the saturation point. Once carbon is saturated, odor will continue to carry through the filters.

Service Life of Adsorbents

Service life of an adsorption system, using activated carbon, for purposes of replacement may be computed from the following formula (Fig. 4).

$$\text{Time of service life (hr.)} = \frac{6.43(10)^6 SW}{e\,Qr\,M\,Cv}$$

Where S = ultimate proportionate saturation of carbon or fractional retentivity; W = weight of carbon (lb.); e = fractional adsorption efficiency; Qr = cfm. of air processed by adsorption equipment; M = average molecular weight of contamination; Cv = ppm. of contaminants.

The following are the properties of some atmospheric contaminants:

	Mol. Wgt., M	Retentivity S	Odor Threshold Conc., ppm.
Acrolein (heated fats)	56	0.15	1.8
Hexane	86	0.16	Almost odorless
Phenol	94	0.30	0.28
Valeric acid (body odor)	102	0.35	0.00062

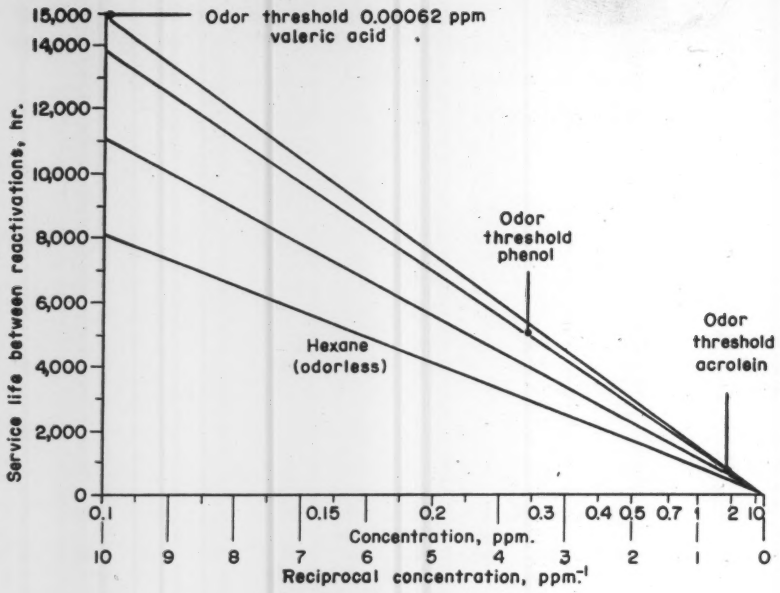


Fig. 4. Life of carbon adsorption equipment.

With heavier molecular weights, when concentration exceeds about 2 to 5 ppm. of air stream, service life of activated carbon is greatly diminished. This calls for frequent reactivations and correspondingly high operating cost.

Equipment Used With Carbon

One satisfactory arrangement for activated carbon is in small cylindrical canisters where 6-14 mesh carbon is held between concentric perforated cylinders. Each canister holds ¾-1½ lb. of carbon and each can handle 25-35 cfm. of air. A number of canisters are placed in a manifold. For large air flows, carbon is held in thin beds between screens or perforated sheets of metal. Air must be reasonably free of solid and liquid particles.

Carbon canisters have proved successful in preventing the escape of a tenacious garlic-sulfide stench in a pharmaceutical plant. Installation consists of 503 canisters each with 1.5 lb. carbon, handling 12,000 cfm. Carbon is reactivated every six months.

It has been observed by Turk[6] that the upper practical range for activated carbon application (2 to 5 ppm.) is far below the lower practical range for catalytic combustion (1,000-1,500 ppm.) and that this void has not been stressed in current literature.

A great number of industrial plant stack exhausts emit odors in quantities between these two ranges. In this area consideration should be given to odor masking and odor counteraction.

ODOR MASKING METHODS

Odor masking is the process of eliminating the perception of one odor or a group of odors by superimposing another odor or a group of odors to create a new odor sensation, preferably pleasant.

Odor control chemicals used for masking purposes are those aromatic chemicals and their byproducts which are derived chiefly from synthetic aromatic chemical manufacture. A masking agent does not alter the composition of pre-existing odor. When superimposed it is selected by the nasal perception apparatus as long as there is sufficient presence of the masking odor in the air stream.

Organic odor control chemicals are numerous. Each type differs, since some may be malodorous and others sweet or sour, fresh or musty. Examples are vanillin, methyl ionones, eugenols, benzyl acetate, phenylethyl, alcohol, heliotropin. Only by selected manufacture and measurement is it possible to obtain an odor control chemical suited to a particular masking or odorization problem.

Many odor nuisances fall into similar patterns for similar operations in the same industry; odors from a sulphate pulp mill, from rayon processing, asphalt blowing and many of the chemical processes. In many cases, where the basic character of the operation is known, a sample of the odor effluent is not necessary to establish a suitable odor masking or modification compound.

In spite of the fact that all normal people can perceive odors and many people find some odors agreeable, odor masking (and in its turn, odor counteraction) is not a field for amateur experimentation.

People suffering from brain lesions, injured olfactory nerves or obstructed nasal passages may be anosmic. Substances of different chemical constitution may have similar odors. Quality, as well as the strength of the odor, may change on dilution. The sense of smell is rapidly fatigued. Fatigue for one odor will not affect the perception of other dissimilar odors but may interfere with the perception of similar odors.

Formulation of a preferred odor control medium requires a great deal of delicate osmic analysis and technical know-how. Completed formulation must include, in addition to maximum odor strength and optimum odor quality, special properties of chemical stability, lasting power and physical form.

How to Apply Compounds

In comparison with the laboratory experience required to formulate odor masking compounds, application is relatively simple and does not require excessive capital investment.

For certain processes, such as digester operation in the kraft sulphate process, or cooking meat scraps and bones in rendering plants, odor masking compounds are added directly to the cook. This method of treatment requires no investment in mechanical equipment, although the trend is toward adding the masking compounds automatically with proportioning pumps. Concentrations may range from 10 to 50 ppm. based on the weight of the process charge under treatment.

Odor masks may also be applied by air or pressure atomization (through properly designed spray nozzles) of a dilute dispersion of the material into the stack from which

malodors are normally discharged (Fig. 5). If the odor masking agent is water soluble it can be diluted with water to most practical dilutions, usually 1 to 5%. Injection is usually at a point well below the top of the stack to assure good mixing with the effluent vapors.

An oil-base masking agent may be sprinkled along the shoreline of a lagoon or poured on the liquid surface of the lagoon where it will spread most readily. Normal evaporation under the heat of the sun vaporizes the mask continuously along the entire area.

Pros and Cons of Masking

Masking compounds should never be used to mask or cover up a toxic concentration of gas. Many odorous compounds such as hydrogen sulphide are highly toxic and non-recognition of the odor in sufficient concentration may be fatal.

Advantages of the use of masking agents are minimum or no capital investment required for equipment; ease of application; relatively low cost in comparison with mechanical equipment; immediate availability for known odor nuisances.

Extreme care must used in handling. Spillage or contact on hands or clothing may create objectionable odor concentrations. Even pleasant odors may be objectionable in high concentrations. For this reason application of odor masking compounds must not be so great in quantity that the resultant combination may itself be objectionable.

Odorimetric methods for determination of odor strength of odorous chemicals have been described and the expressions of Scent Unit, Scent Value, Cent-Scent Value established. A method for determining masking strength is explained by Tremain.[9]

Control Via Odor Masking

In preparation for odor masking control take these basic steps:

- Make an analysis of the toxic materials or lack of toxic materials in ppm. and total cfm. from stack exhausts. Check with the local public health officials or air pollution officers to determine whether dispersal of these materials is well below the minimum permissible level in the surrounding area.
- Do not attempt to formulate masking compounds unless you have had considerable and lengthy experience in odor chemistry.
- Establish quantities of material used in process, particularly the odorous materials, and temperatures of process and stack effluent. Call in a competent manufacturer of masking compounds and disclose as much information regarding the process as is permissible. Have him observe the malodors from the stack exhaust and in the surrounding area.
- If the masking compound is to be used as an additive, establish in the laboratory that the addition has no effect on the process. If the masking compound is to be applied to the stack exhaust, it is advisable to perform a laboratory or pilot-plant experiment with the product to establish ratios which will not result in an intense effluent. Determine that an offensive conclusion might not result in the final combination as a consequence of odor incompatibility.
- Install equipment as prescribed by the masking compound manufacturer. This is ordinarily a simple installation that can be made by plant personnel and usually involves only a source of air and a calibrated spray nozzle.
- By means of an odor jury make area surveys over a period of several days. Take into consideration known factors regarding air inversions, topography and wind movements. Care should be used in building up to the required concentration, since an excess may result in complaints in the surrounding area regarding new odors.

ODOR COUNTERACTION METHODS

Zwaademaker was probably the first odor researcher to study the counteracting effect of two dissimilar odors.[10]

The principle of odor counteraction is separate and distinct from the psychological effect of odor masking. In odor masking strong odors tend to mask weaker ones. If the two odors are of about equal strength a blend of the two is observed and both can be identified. If one is considerably stronger than the other, it alone as a rule, is perceived.

In odor counteraction certain pairs of odors in appropriate relative concentrations are antagonistic. When the two are sniffed together both odors are diminished. Various pairs of counteracting odorous substances were recorded by Zwaademaker in 1895. He used a device to individually introduce into either nostril odorous substances in a ratio of quantities required for counteraction.

Many other workers, including Moncrieff and Bachman, have made similar studies in which it was possible to compensate the olfactory effects of various chemicals to a point

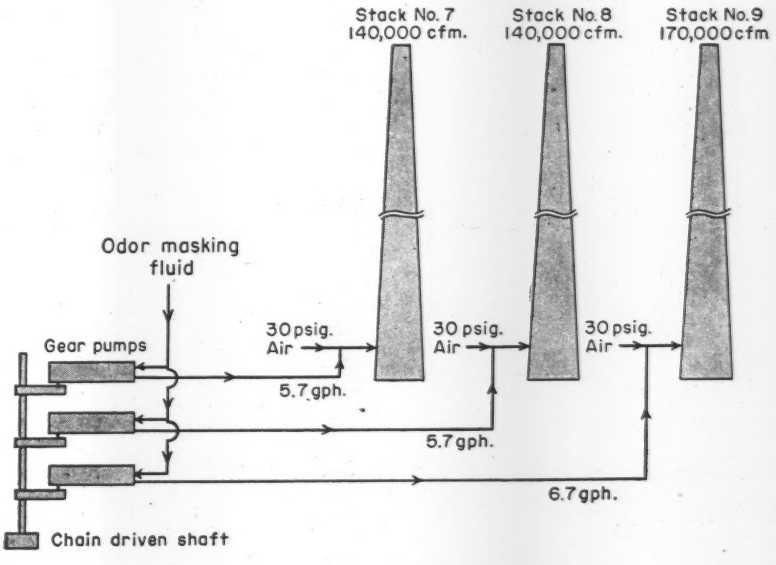


Fig. 5. How to inject odor masking compounds.

of total odor disappearance or significantly close to the point of total odor disappearance. It is a known fact that in the group benzene, toluene, xylene, pseudocumene and durene, combinations in the correct proportions from this group can be produced which are almost odorless. Many materials are thus available for odor counteraction, including the essential oils.

Odor counteraction, as developed to date, is based on significant work done by early experimenters. Development of odor counteractants is a pure matter of Edisonian research and many years have been spent in this delicate work by competent odor researchers.

Impetus Comes From Air Conditioning

Odor counteraction was first applied in the air conditioning industry. Household products such as oil cloth and rubber, polishes, wax, paints, inks and insecticides are all antisocial from an odorous standpoint.

The air conditioning industry, in a combined attempt to improve atmospheric control, was faced with a serious problem. Attempts to dominate these odors by the use of sassafras, wintergreen, citronella, pine, lavender and other compounds were not satisfactory. Commercial use of odor counteraction thus developed in this field. Since air freshness was desired, instead of recognizable specific odor types, odor counteraction with a sense of fresh air was developed by introducing traces of the chemicals found in outdoor plant-life areas (chlorophyll). This work was extended to the industrial odor control field.

Although an industrial process may be simple, industrial odors coming from the process may be a complex group of odors. It is unusual to obtain a specific odor from an industrial process stack. Even when this is the case the odor may combine with transient odors in the surrounding atmosphere. For this reason industrial odor counteractant formulations, although designed for specific odor descriptions, may contain complex groups of odor counteractants.

There is no chemical method known for the determination of the effectiveness of odor counteractants. Effectiveness can be determined by actual odor perception. In the last analysis this is the criteria for the effectiveness of any odor abatement method.

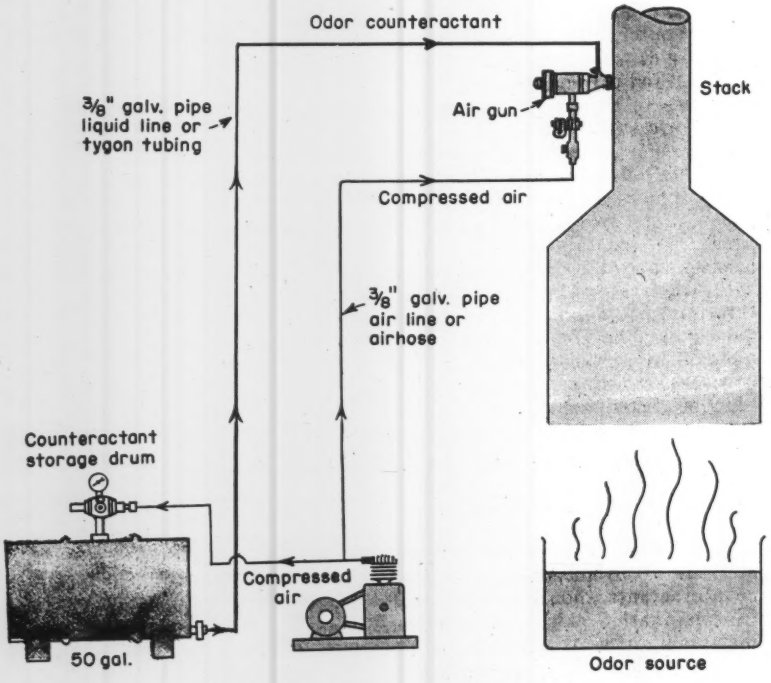


Fig. 6. How to inject odor counteractants.

How Does Counteraction Work?

Odor counteraction deals with molecules of odor. For practical purposes an odor is always a gas molecularly dispersed in air in sufficient concentration to be above the threshold level of perception. For this reason odor counteractants are most effective when vaporized and combined with the air stream by molecular dispersion.

Stream exhaust can be held to the ground by air inversion, vertically dispersed, or horizontally dispersed. But the odor counteractant is carried with a malodor and is noticeably effective until the odor is dispersed beyond the range of perceptibility.

Applying Counteraction Compounds

Odor counteraction is particularly effective against multiple odor sources. There may be literally hundreds of sources of odors within a plant proper: main stack, ventilation of process areas, vents from storage tanks and chests, spillage areas, wet walls, stock piles, all contribute to the total industrial odor load.

Odors from this source expand by molecular dispersion in a rough range from 5 to 1 until the odorous pool is taken over by general air movement. Further dispersal, mixing and dilution, takes place during the variable air movements until the characteristic odor of the plant is perceived in the complaining area.

Odor counteractants are vaporized by atomizing the counteractant into the air movement or stream by means of a calibrated atomizing nozzle. These vaporizing points are usually located in or near the stack exhausts but may also be located at the plant roof top and in the vicinity of most odorous effluents (Fig. 6). This provides vertical coverage from the bottom to the top of the odorous pool leaving the plant.

Counteractants mix with the odorous air stream by molecular dispersion and air movements and are designed to follow the physical behavior pattern of the odorous elements. Some odorous elements disperse beyond the limits of perceptibility rapidly, others are tenacious and do not disperse horizontally or vertically as quickly thus creating special control problems.

Odorous discharge from kraft sulphate pulp mills, probably due to some microscopic particulate forma-

tion, continue to travel and vaporize for miles. Specific odor counteractants have been designed to follow these physical dispersal patterns.

Vaporization of a liquid odor counteractant is accomplished by clean compressed air (approximately 2 cfm./gun). The liquid odor counteractant is stored in a pressure drum at a convenient location and fed through small connecting lines to the vaporizing nozzles by air pressure.

Operation is automatic and once the installation is set up and balanced requires little maintenance except for weekly filling of the pressure containers. Odorous sources vaporizing at a continuous rate are treated continuously. The intermittent operation of relief valves may be treated during the blow off by automatic valves which operate according to the time of blow off. Equipment is easy to install and no alterations are required to process equipment. No down time is required for installation.

Counteraction: No Cure-All

Since there is no chemical effect on the odorous effluent, odor counteractants should not be used in combination with highly toxic materials unless the dispersal rate is well below the maximum permissible level. General method of application has the important practical advantages of very little initial equipment costs, negligible space requirements, and greater freedom from the necessity of confining the atmosphere into a close space for treatment.

There is no universal odor counteractant. Odor counteraction formulas are designed for specific groups of odors. Odor counteraction installations should be made by a specialist who can discriminate between odors and estimate the intensity of concentrations involved in the problem.

Although it is rather easy for the trained odor expert to identify characteristic odors, it is necessary in some cases to decrease or increase an odor by 20 to 50% before the nose can consistently detect the difference. For this reason it is usual in application to operate for 20 or 30 days with an odor counteractant to determine minimum amount necessary to take care of all variations of odor level and to establish an exact cost of operation.

The more intense a specific malodor may be, the more odor counteractant is required for effective operation. Any odor counteractant used in industrial work areas or industrial stacks for the control of atmospheric odor pollution should be nontoxic, nonallergenic, nonflammable, noncorrosive, chemically inactive, economically feasible and should be effective in the laboratory and in the field.

Odor counteractants cannot be used for the control of particulate material. In extreme examples, where the air-borne waste of an industrial process may contain dust, fume, condensable vapors and uncondensable gases, entrained material should be scrubbed to remove dust and soluble or condensable vapors; then passed through an electrostatic precipitator to capture fume and mist particles too small to be retained in the condenser or scrubber; and finally treated by odor counteractants to reduce the highly offensive character of insoluble noncondensable molecules.

Applying Odor Counteraction

Procedure for getting the best results with odor counteraction is as follows:

- Determine whether present stack effluent is well within the local health or air pollution control requirements for emission of particulate material and toxic gases. Determine cfm. of all stack exhaust gases. Approximate intensity of odorous effluent on a percentage scale for each source. Examine the plant for odorous ventilating areas, wet walls, work areas, and stockpiles.

- Arrange for an odor appraisal survey to be made by an odor counteraction specialist. If the odorous effluent can be reasonably handled, a cost estimate may be in order. Although separate plant processes may be nearly identical, area difference, topography and temperament of the complaining area might require treatments which differ in cost. In either case cost of installation is negligible. A full plant run may be made for a period of 30 days without great expense.

- Arrange for an appropriation for a 30-day trial which will demonstrate effectiveness of the odor counteractant application and will also determine cost of operation on a continuing basis.

- During the 30-day trial period arrange for a competent jury to evaluate results over the entire area.

SUMMARY OF ODOR PROBLEM

Air pollution problems are given more attention in the public press every day. All of the control methods discussed here for odor have proved successful in the field. But each problem is specific and unusual. It is difficult, therefore, to make general cost comparisons between the methods. Each, taking advantages and disadvantages into account, should be considered for any problem.

The Air Pollution Control Assn. with headquarters in Pittsburgh, Pa., has taken a leading part in the battle for clean air. The association is made up of control officials, governmental agents, industrial groups, research groups, educational groups, and others including many international representatives. Its major purpose is to accumulate and disseminate information regarding air pollution control. Through its association meetings, held throughout the country, valuable information regarding the realistic approach to the air pollution problem is disseminated and discussed. The APCA also distributes a monthly abstract of current literature and a journal of proceedings.

References

1. Pendray & Co., N.Y.C., "Opinion Survey on Odors & Fumes as Air Pollution Problems," Mar. 29, 1955.

2. R. H. Sherlock and E. J. Lesher. *Air Repair* **4**, 13-22 (Aug. 1954).

3. R. W. Moncrief. The Chemical Senses. 2nd ed., chapter XII, London, Leonard Hill, Ltd. (1951).

4. C. W. Gruber. Odor Pollution From The Official's Viewpoint. American Society for Testing Materials, Philadelphia, Pa., preprint No. 105A (1954).

5. H. R. Suter. Range of Applicability of Catalytic Fume Burners. *J. Air Poll. Control. Assoc.* **5**, 174-5, 184 (Nov. 1955).

6. A. Turk. Odor Control Methods: A Critical Review. Abstract, annual meeting of the American Society for Testing Materials, Chicago, Ill. (June 1954).

7. McCord and Witheridge. Odors Physiology and Control. McGraw-Hill, New York (1949).

8. Air Conservation Engineering. Connor Engineering Corp. (1953).

9. B. K. Tremaine. *Tappi* **37**, 141A-143A (Aug. 1954).

10. H. Zwaardemaker. Die Physiologie des Geruchs. Leipzig (1895).

Development of an Improved Smoke Inspection Guide*

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Present methods of black smoke inspection generally involve visual observation of the degree of blackness of the smoke as it leaves the source, and comparison to a shade of standard blackness. Although all methods of visual black smoke density observation share many drawbacks[1], these methods are, for economic reasons, the only ones open to most municipal enforcement officials. Standards used by air pollution control agencies are usually of one of 2 basic types: *(1)* Reflectance type, which includes the Ringelmann Chart[2, 3] and smaller card sized versions[4] reproduced to give equivalent shades of blackness; *(2)* Transmittance type [5, 6], including those comparators employing film and other translucent reference slides which are viewed against the sky, generally through a collimating system.

Reflectance and Transmittance Type Standards

The standards of both categories have disadvantages as well as advantages. The major drawback of the reflectance type of smoke inspection guide[1, 6] is that a smoke plume, whose shade of blackness is due primarily to transmitted light, is visually compared to an opaque reference giving only reflected shades of blackness. Variations of the intensity and color of the incident light will vary the relative appearance of the smoke and reference standard. Hence a plume of constant density may under different illumination give quite different Ringelmann values. The principal advantage of the reflectance type is simplicity and low cost.

Transmittance type smoke inspection guides, while overcoming the major drawback of the reflectance type, are at present expensive. The use of translucent reference shades of blackness enables a comparison of the smoke and transmittance guide to be made, based on the same optical principle of operation.

The objective of the present study is to evaluate the performance of both guide types and based on this evaluation to develop a smoke inspection standard embodying the following characteristics: *(1)* The new smoke guide must be simple, inexpensive, and suitable for general field use by smoke inspectors; *(2)* the reference guide should correlate with the black smoke plume under field conditions; *(3)* to be useful to enforcement agencies without requiring extensive revision of legislation, the new guide must be capable of correlating with the nominal standards currently in use.

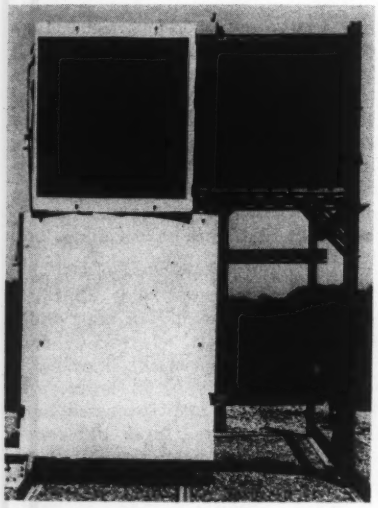


Fig. 1.

Test Apparatus and Procedures

To establish a correlation of the comparator guides to the black smoke under an extreme range of field lighting conditions, a source of smoke was needed which could be maintained constant over extended periods of time. Due to the fluctuating nature of combustion smoke, a simulated smoke standard was developed which exhibited the same optical behavior as black smoke under field lighting conditions. It consisted of an aqueous suspension of colloidal carbon contained in a clear Lucite cell 3 in. thick and 24 in. on a side (Fig. 1). The use of such a controlled *smoke* removed one of the major variables encountered in the field and permitted a direct evaluation of the guides for changes in lighting conditions.

The selection of the guides used in the study was based on their availability and ease of manipulation. The U. S. Bureau of Mines Ringelmann Chart was chosen as representative of the reflectance type guide, and exposed photographic film as representative of the transmittance type guide.

Preliminary Investigation

In practice the inspector's evaluation of a smoke involves a subjective judgment. The influence of psychological factors such as learning, light contrast, and environmental interferences makes necessary a statistical treatment of the data for a proper test evaluation. A preliminary statistical study was made to evaluate the performance of a film type guide as compared to a Ringelmann type chart. Tests were performed in the laboratory using simulated smoke, controlled lighting and background conditions, and a panel of 4 observers selected from a group of six sub-

* Presented at 50th Annual Meeting of the Air Pollution Control Association, June 2-6, 1957, St. Louis, Mo.

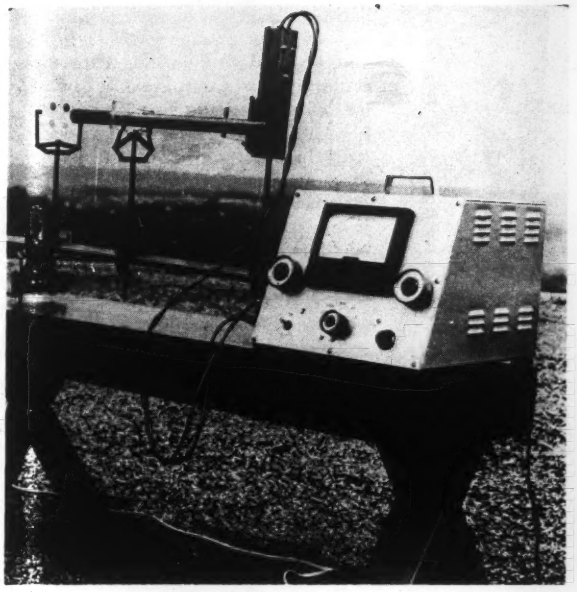
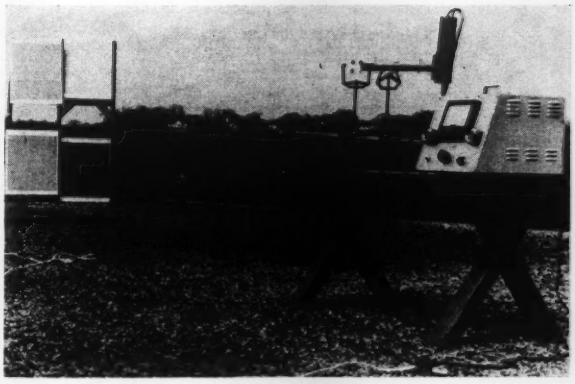


Fig. 2 (Left).

Fig. 3. (Below).



jects tested. The results demonstrated better correlation between the smoke and film values and greater stability of the film readings under these conditions.

For a performance evaluation of the guides under field conditions, the present study was conducted under atmospheric illumination. To eliminate the subjective elements inherent in the preliminary study, objective measurements were made using photometric instrumentation.

Apparatus and Procedures

The instrumentation used in this investigation is shown in Fig. 2. A photometer (Photovolt, Model 520-M photomultiplier) selected for its high sensitivity was used in taking all light intensity readings. This instrument will measure luminous flux over 4 decimal ranges extending from a minimum of 5×10^{-8} to 5×10^{-3} ft. candles. To determine the amount of light transmitted by the smoke or film strip or reflected by the Ringelmann Chart, it was necessary to limit the light reaching the photometer to that emanating from the specific areas under observation. For this purpose, a collimating tube was constructed which permitted a maximum scanning angle of 1.6°. A sighting tube mounted on the barrel of the collimator permitted accurate selection of the areas to be scanned.

In the experiments the instrument was set facing approximately north, with the collimator sighted just above the horizon. The smoke standard and Ringelmann Chart were placed 50 ft. in front of the instrument at a height determined by its line of sight (Fig. 3).

At 50 ft. the collimator subtends a field of view 17 in. in diam. To provide this necessary area, the Ringelmann Charts as well as the standard smoke cell were made a minimum of 24 in. on a side. The Ringelmann Charts were prepared by cutting and mounting 12 of the 6 by 9 in. published charts on large pieces of white poster board. The smoke cell and chart to be studied were mounted on a frame which was set normal to the instrument line of sight.

The film guide tested consisted of small film strips of the same neutral coloration as the standard smoke, and for testing purposes was mounted 1 in. from the end of the collimator. This distance was 19 in. from the photomultiplier and corresponds to the approximate distance the chart would normally be held from the eye. Preliminary tests proved that the observed transmission of the film remained essentially constant for the instrument independent of the distance.

In conducting the performance tests, light intensity readings were taken at ½ hr. intervals between 11:00 A.M. and 5:00 P.M. To obtain a complete set of readings, light intensity was measured as received from the film, the smoke, the Ringelmann Chart, and the adjacent sky background. During tests conducted in clear weather, a transit set along the projected axis of the collimator was used to determine the position of the sun at the time of each set of readings.

Smoke Standard Verification

Atmospheric illumination is both a complex and variable system, consisting of diffuse sky light and direct sunlight. The relationship of this complex system to the light properties of a black smoke plume will depend on three conditions: first, the degree of overcast or haze as it affects the intensity and constancy of diffuse light; second, the intensity and orientation of the incident sunlight; and third, the variance of intensity ratios of diffuse to direct light.

An evaluation of the relationship of the physical to the optical characteristics of the black smoke plume under atmospheric illumination indicates: first, the suspensoids comprising the black plume, are predominantly solid carbon particles which are opaque and have extremely low reflectance; second, the particle size spectra lie above the size range necessary to produce significant light interference phenomena. Consequently, under conditions of atmospheric illumination, the plume can be expected to exhibit the optical properties of low light scattering and high light absorption.

In order that the performance of the 2 guide types be studied under conditions which are representative

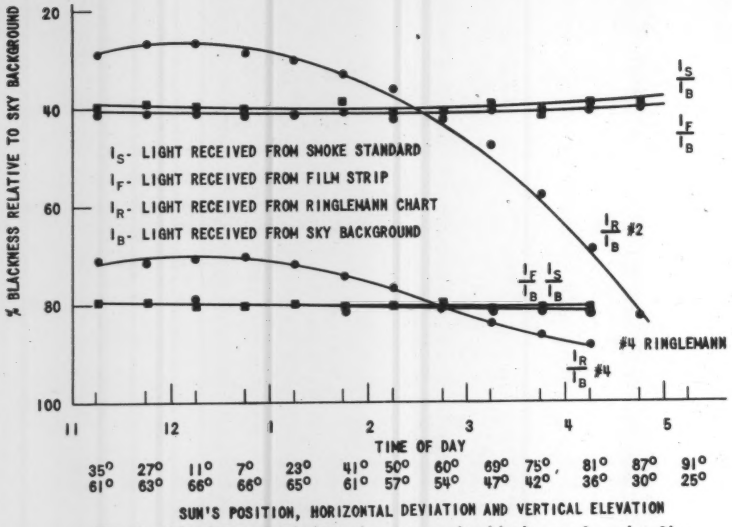

% BLACKNESS RELATIVE TO SKY BACKGROUND
20
40
60
80
100
I_S- LIGHT RECEIVED FROM SMOKE STANDARD
I_F- LIGHT RECEIVED FROM FILM STRIP
I_R- LIGHT RECEIVED FROM RINGLEMANN CHART
I_B- LIGHT RECEIVED FROM SKY BACKGROUND
$\frac{I_S}{I_B}$
$\frac{I_F}{I_B}$
$\frac{I_R}{I_B}$ #2
$\frac{I_F}{I_B}$ $\frac{I_S}{I_B}$
#4 RINGLEMANN
$\frac{I_R}{I_B}$ #4
11 12 1 2 3 4 5
TIME OF DAY
35° 27° 11° 7° 23° 41° 50° 60° 69° 75° 81° 87° 91°
61° 63° 66° 66° 65° 61° 57° 54° 47° 42° 36° 30° 25°
SUN'S POSITION, HORIZONTAL DEVIATION AND VERTICAL ELEVATION

Fig. 4. 4/30/57 and 5/1/57, clear sunny sky, blackness of smoke, film, and Ringlemann chart relative to sky background.

of actual field conditions, it is necessary that the simulated smoke standard exhibit the same optical characteristics as a plume itself. The suspensoid used in the smoke standard was colloidal carbon, which is opaque and has low reflectance. The physical difference between the suspensoids in a plume and the colloids which may affect their optical characteristics is the comparative particle size spectrum of each. Absorption measurements of the smoke standard employing a Beckman spectrophotometer Model B gave essentially equal values over the range of visible light from 4500 to 6500 Angstroms, thus indicating no significant light interference effects. As a result it was concluded that the particle size spectrum was not critical and the standard possessed optical properties equivalent to those of black smoke.

Experimental Results

Because of the complexity and variability of the atmospheric illumination system, an empirical approach was used in studying the reflection and transmission guides chosen for evaluation. Comparisons of the guides were made for 2 degrees of blackness, the first at an equivalent Ringelmann Number 2 and the second at an equivalent Ringelmann Number 4. These levels were chosen to cover a sufficient range in degree of blackness to arrive at a practical evaluation of the behavior trends over the entire range.

Two practical methods of application of smoke inspection guides are possible under field conditions: *(1)* an indirect comparison of blackness of the guide relative to the sky background to that of the smoke plume relative to the sky background; *(2)* a direct comparison of the blackness of the guide to that of the smoke plume. Therefore, evaluation of the experimental data is presented in terms of both methods. Since all evaluations are on a comparative basis, essentially simultaneous measurements were made of the light received from each type of guide under identical atmospheric illumination.

The first phase of the study covers the evaluations made from data obtained during clear (no clouds, no haze) sunny days representing periods of ideal atmospheric illumination in which the intensities of direct and diffuse light varied uniformly. Results, according to the first meth-

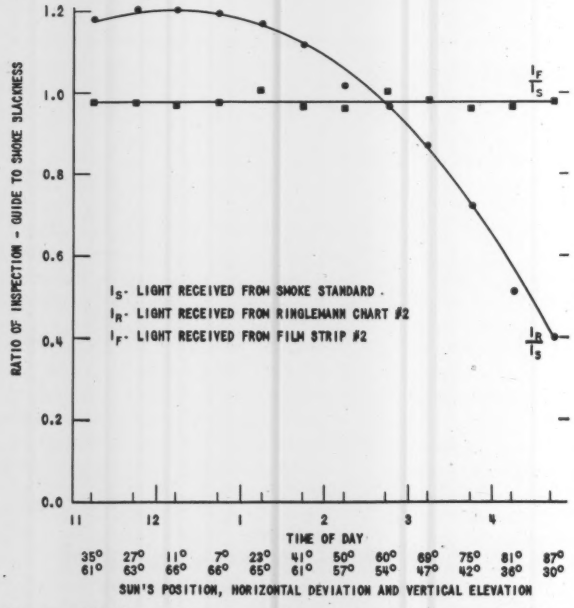

RATIO OF INSPECTION - GUIDE TO SMOKE BLACKNESS
1.2
1.0
0.8
0.6
0.4
0.2
0.0
I_S- LIGHT RECEIVED FROM SMOKE STANDARD
I_R- LIGHT RECEIVED FROM RINGLEMANN CHART #2
I_F- LIGHT RECEIVED FROM FILM STRIP #2
$\frac{I_F}{I_S}$
$\frac{I_R}{I_S}$
11 12 1 2 3 4
TIME OF DAY
35° 27° 11° 7° 23° 41° 50° 60° 69° 75° 81° 87°
61° 63° 66° 66° 65° 61° 57° 54° 47° 42° 36° 30°
SUN'S POSITION, HORIZONTAL DEVIATION AND VERTICAL ELEVATION

Fig. 5. 4/30/57. Clear sunny sky. Ratio of inspection guide to smoke blackness.

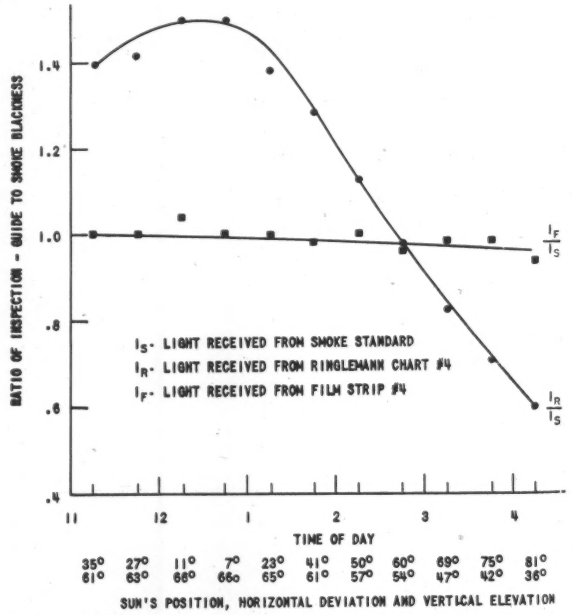

RATIO OF INSPECTION - GUIDE TO SMOKE BLACKNESS
1.4
1.2
1.0
.8
.6
.4
I_S- LIGHT RECEIVED FROM SMOKE STANDARD
I_R- LIGHT RECEIVED FROM RINGLEMANN CHART #4
I_F- LIGHT RECEIVED FROM FILM STRIP #4
$\frac{I_F}{I_S}$
$\frac{I_R}{I_S}$
11 12 1 2 3 4
TIME OF DAY
35° 27° 11° 7° 23° 41° 50° 60° 69° 75° 81°
61° 63° 66° 66° 65° 61° 57° 54° 47° 42° 36°
SUN'S POSITION, HORIZONTAL DEVIATION AND VERTICAL ELEVATION

Fig. 6. 5/1/57. Clear sunny sky. Ratio of inspection guide to smoke blackness.

od, relating percent blackness (defined as the light intensity received from the smoke standard or guides divided by the light intensity received from the sky background) of the inspection guide and the smoke standard relative to the sky background (Fig. 4) show 3 significant facts: *(1)* the percent blackness of the smoke standard is independent of the sun's orientation and of the variation in its illumination intensity; *(2)* the percent blackness of the film strip correlates with that of the smoke standard and is, furthermore, independent of the variations in the illumination system; *(3)* the percent blackness of the Ringelmann Chart, however, is dependent on the orientation of the sun and on the variation of its illumination intensity. Although the variation in the percent blackness of the Ringelmann Chart is uniform, it is not predictable under field conditions.

When the results are evaluated on the basis of a direct comparison, they are expressed as a ratio of absolute values of light intensity received from the guide to corresponding values from the smoke standard (Fig. 5, 6). The results again verify the excellent correlation of the degree of blackness of the film strip with that of the smoke standard through varying light conditions as indicated by a maximum deviation of 4.2%. Since the degree of blackness of the guides relative to that of the smoke standard is shown as a ratio, it can be expressed as a percentage deviation. On this basis there is indicated a trend which shows that, under conditions of ideal atmospheric illuminations, the percent deviation of the Ringelmann Chart increases with the degree of blackness of the smoke standard.

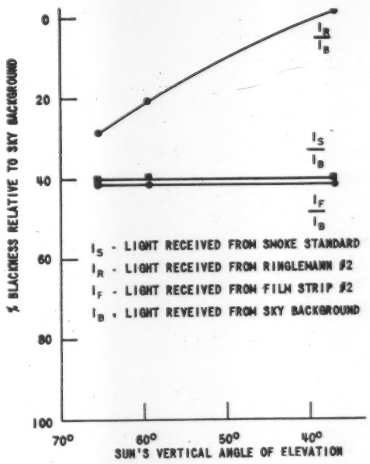


Fig. 7. 4/30/57. Blackness of smoke, film, Ringlemann relative to sky background.

A further evaluation of the performance of the guides was made based on an experiment in which the horizontal component of the angle of incidence of the direct sunlight to the guides was held constant at zero degrees, and the vertical component of the angle of incidence was allowed to vary as the sun approached the horizon (Fig. 7). The conclusions previously reached regarding the constancy of the film guide and the variability of the Ringelmann Chart continued to hold under these special lighting conditions. In this case, however, the Ringelmann Chart shows a decreasing percentage blackness as the sun's position approaches the horizon (angle of incidence of the direct sunlight to the guide surface approaches zero). In the previous case, however, where the guides were oriented with the normal running north and south, the percentage blackness increases as the sun approaches the horizon. This difference in behavior can be explained in terms of the cosine law of illumination, which states the illumination of a surface varies directly as the cosine of the angle of incidence of the direct light to the surface. When only the vertical component of the angle of incidence of the direct sunlight to the guides decreases, the horizontal component being held constant at zero degrees, the illumination increases since the absolute angle of incidence approaches zero. When again considering the first case, in which the chart normal was oriented north and south, the horizontal and vertical components of the angle of incidence of the direct sunlight to the guides were both allowed to vary with the sun's movement. In this case the illumination decreases since the absolute angle of

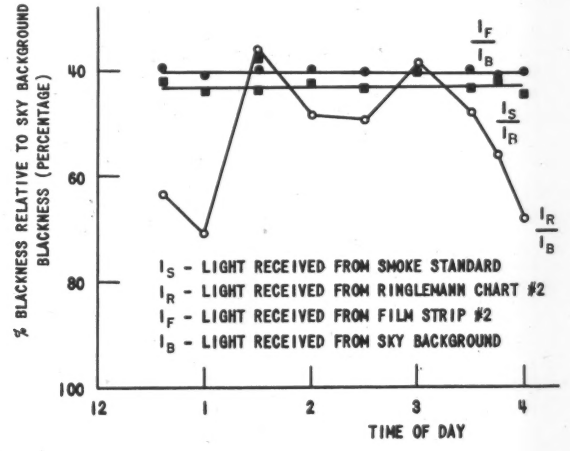


Fig. 8. (Above) 5/8/57. Blackness of smoke, film, and Ringlemann chart relative to sky background-broken clouds overcast.

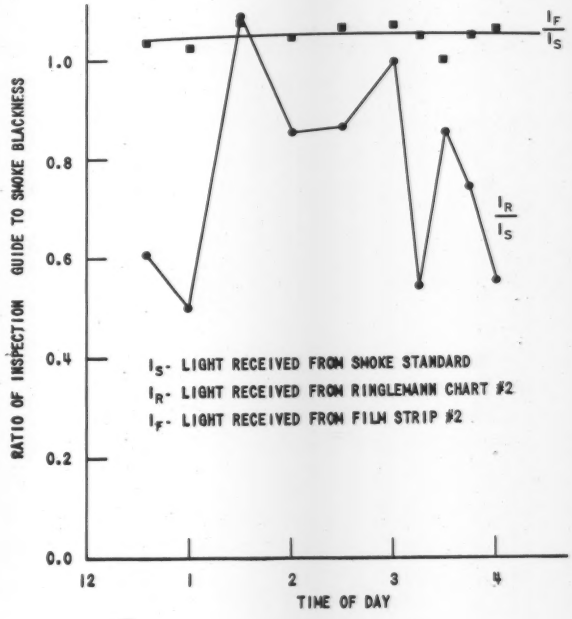


Fig. 9. (Right) 5/8/57. Ratio of inspection guide to smoke blackness, broken clouds overcast.

incidence increases as the sun's position approaches the horizon.

The general effects of the orientation of the guides are observed from these two special cases. First, the orientation of the film or transmittance type guide has no significant effect on the constancy of the results. Second, the orientation of the Ringelmann Chart or reflectance type guide affects the resultant light intensity or degree of blackness. Fundamentally, the orientation of the reflectance type guide results in varying degrees of blackness, either greater or less than the nominal values specified, depending on the angle of incidence of the direct sunlight to the guide, which is established by the orientation of the guide.

The second phase of the study covers the evaluation made from data obtained during a day of cloudy overcast with occasional breaks in the clouds. This was a period in which the configuration of the cloud cover and, hence, the over-all illumination pattern varied continuously. Readings were not taken, however, during intervals of direct sunlight on the guides. The effects of atmospheric illumination when evaluated on the basis of either a direct or an indirect comparison (Fig. 8, 9) show 3 significant facts: *(1)* Random variations in atmospheric lighting have no effect on the constancy of percentage blackness of the smoke standard; *(2)* the degree of blackness of the film strip correlates with that of the smoke standard and is independent of variations in illumination system; *(3)* the Ringelmann Chart is dependent on the random diffuse background and foreground sky light. Furthermore, under broken cloudy conditions there does not appear to

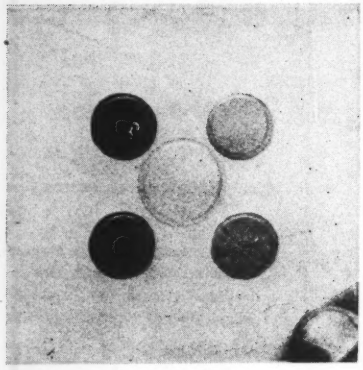


Fig. 10.

be any trend correlating with the sun's position that would correspond to the trend of effects of direct sunlight observed in the first phase of the study.

Guide Development

It is realized that all visual comparator type guides have an inherent limitation in that equal optical densities of black smoke plumes do not necessarily reflect equal contaminant discharge to the atmosphere. The advantages, however, of rapid and simple application offset this limitation and make this method a practical enforcement tool. For these reasons it is felt that the development of a smoke guide which is simple, inexpensive and suitable for general field use, and which correlates with the black smoke plume under field conditions, would be most useful.

A prototype guide was developed utilizing exposed photographic film strips (Fig. 10). The selection of a transmittance type guide was made based on performance results. Percent blackness values were chosen corresponding to the nominal Ringelmann Chart values for 2 reasons: first, to permit the use of the guide without extensive revision of legislation; second, the nominal Ringelmann values have been shown to occur under specific conditions of atmospheric illumination. Enforcement agencies will be given the opportunity to field test prototype guides as a continuation of this study. Evaluation of various forms of the guide will be made to determine ease of application, stability, and effect of environmental interferences. A final version of a transmittance type guide will be based on these field evaluations.

Acknowledgment

The authors acknowledge the contribution of Dr. M. W. Bredekamp, Mr. J. L. Witherow, and Mr. K. A. Busch, who conducted the preliminary statistical guide evaluation during the summer of 1956.

References

1. Lionel S. Marks. Inadequacy of the Ringelmann Chart. *Mechanical Engineering,* ***681*** (Sept. 1937).
2. Max Ringelmann. Methode d'Estimation des Fumees Produites par les Foyers Industriels. *La Revue Technique,* ***268*** (June 1898).
3. Rudolph Kudlich. *Ringelmann Smoke* Chart. Bureau of Mines Information Circular 7718, (Revised Aug. 1955).
4. Anon. Power's Micro Ringelmann: A New Aid to Smoke Inspectors. *Power,* **98**: 90, (March 1957).
5. American Society of Mechanical Engineers; Power Test Code 19, Supplement on Instruments and Apparatus, Part 20, Smoke Density Determinations, (1954).
6. John P. Strange. The Smokescope; Paper No. 53-S-3. Presented at the Spring Meeting of the American Society of Mechanical Engineers, (April 1953).

Field Evaluation Of An Improved Smoke Inspection Guide*

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The need for an inexpensive and reproducible method of evaluating black smoke-plume densities has long been recognized by industry and air pollution enforcement agencies. Two types of guides currently in use are the reflectance and the transmittance types. Reflectance types have been shown by previous work of the authors to be nonreproducible since their source of illumination differs from that illuminating the smoke plume. Transmittance guides, employing the same source of illumination, correlate well with plume density. Results of this previously reported work demonstrated two significant facts: (1) the percent blackness of the transmittance type guide correlated with that of the smoke standard and was furthermore independent of variations in the illumination system; (2) the percent blackness of the reflectance type guide was dependent on the orientation of the sun and on variations in its illumination intensity.

Guide Development

It is understood that all visual comparator type guides have an inherent limitation in that equal optical densities of black smoke plumes do not necessarily reflect equal contaminant discharge. The advantages, however, of rapid and simple application offset this limitation and make this method a practical enforcement tool. For these reasons the development was undertaken of a simple, inexpensive transmittance type smoke guide which would correlate with black smoke plumes under field conditions.

Atmospheric illumination is a complex and variable lighting system consisting of diffuse sky light and direct sunlight. Since this complex system of atmospheric illumination differs significantly from the relatively simple system of illumination employed in determining standard film strip densities as supplied by the Eastman Kodak Company, an empirical evaluation was undertaken to establish a correlation between the transmittance values used in the guide development and those used in determining standard film strip densities *(Fig. 1)*. This approach permitted specifications to be given in terms of manufactured film density standards. Density values calculated from the empirical readings of transmission were higher than the Eastman Kodak Company standard densities. The difference was significant and verified the necessity of evaluating film transmission for the same conditions under which the guides will be used.

The instrumentation used in this correlation was similar to that employed in the initial investigation *(Fig. 2)*. A photometer (Photovolt Model 520-M Photomultiplier), selected for its high sensitivity, was used for all light intensity readings. To determine the amount of light transmitted by the film strip, it was necessary to limit the light reaching the photometer to that emanating from the specific area under observation. For this purpose a collimating tube was constructed which permitted a maximum scanning angle of 1.6°.

For testing purposes the standard film strips were mounted one inch from the end of the collimator. This distance was 19 in. from the photomultiplier and corresponded to the approximate distance the guide would normally be held from the eye. Preliminary tests showed that the observed transmission of the film remained essentially constant for the instrument independent of distance.

During the correlation tests, light intensity was measured as received from the film and the adjacent background, the ratio giving transmission readings for each density of the standard film strips. Correlation data was used to establish specifications on standard density values equivalent to the transmittance values desired.

The form of the guide *(Fig. 3)* was a compromise between cost and factors involving possible interferences, ease of operation, durability, and available manufacturing techniques. Percent transmission values were chosen to correspond to nominal Ringelmann Chart values to permit use of the guide without extensive revision of legislation. On this basis 24 prototype guides were purchased to specifications allowing

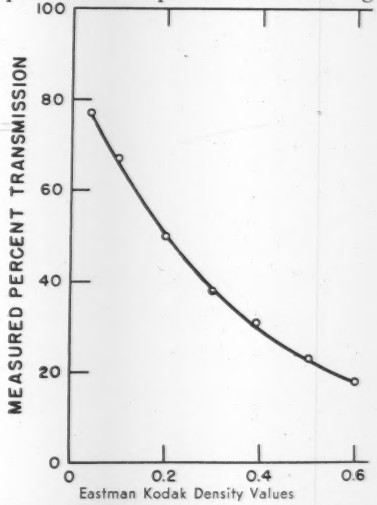

Fig. 1. Photometric measurement of Eastman Kodak standard film strips.

*Presented at the 51st Annual Meeting of the Air Pollution Control Association held at the Hotel Sheraton, Philadelphia, Pa., May 25-29, 1958.

a tolerance of ± 3% of standard film strip densities.

Calibration

Empirical transmission measurements were made under atmospheric illumination for the calibration of the prototype guide. The same instrumentation and procedures were employed as those which were used in establishing the correlation between empirical percent transmission and standard film strip densities. The specified transmission values of 80% and 60% were not realized while the transmission values of 40% and 20% were as specified *(Table 1)*. The actual transmission values of 78% and 62% respectively were not considered significantly different from the specified transmission values to affect materially the field evaluation. This discrepancy can be corrected in future guides.

The calibrated prototype guides were numbered for identification and distributed to air pollution enforcement agencies for field use. Sets of four guides each were sent to six enforcement agencies, two of them in the West Coast area, one in the Great Lakes area, two in the Middle West area, and one in the Southeast area of the country. This random distribution was used to offset the effect of any specific use bias peculiar to an area.

TABLE I

Smoke Guide Transmission Evaluation
(Average values for 24 guides)

Nominal Ringelmann No.	Before Use		After Use		% Transmission Ratio After Use/Before Use
	% Trans.	Std. Dev.	% Trans.	Std. Dev.	
1	78.0	0.5	76.5	0.3	98.1
2	62.3	0.3	60.9	0.7	97.8
3	40.2	0.3	39.3	0.8	97.8
4	20.0	0.1	20.0	0.5	100.

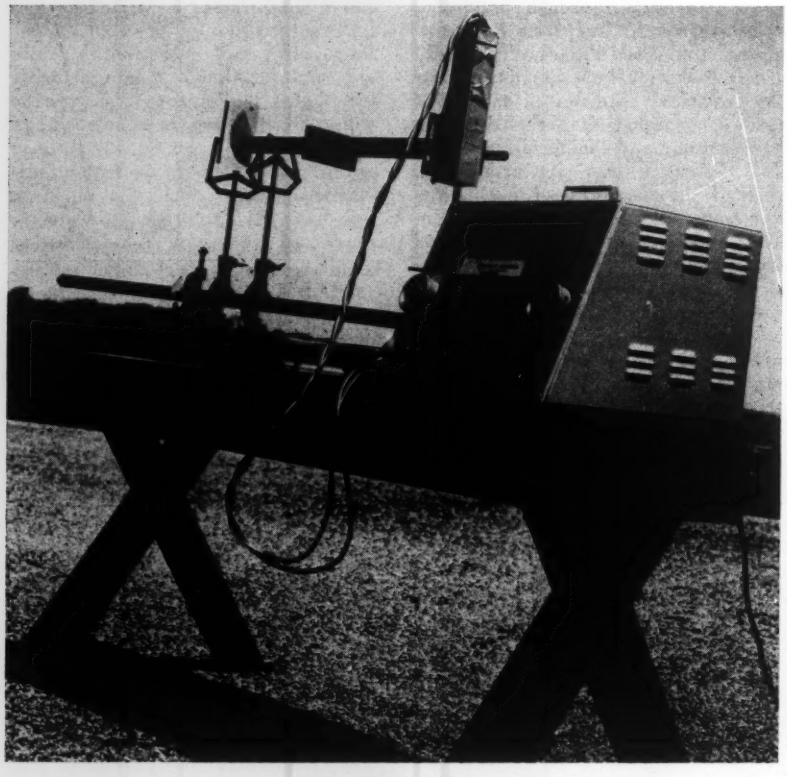

Fig. 2

Field Application

Each guide was field tested by an individual air pollution inspector in accordance with a set of instructions based on guide limitations and giving complete procedures for use and maintenance. The field-test interval for each set of guides was approximately four months' duration (January through April). Subsequent to the field test, personal interviews were held with each of the inspectors assigned for field testing. A questionnaire designed for statistical analysis was then completed based on the response of each individual air pollution inspector. These interviews further allowed judgment to be made of any bias which may have existed as to the use of a new smoke measurement technique.

Analysis

Transmission measurements, before and after use *(Table I)* were made to determine the effect of field use on guide performance. Since frequency of use varied during the four-month period over a range of 10 to 400 applications, an analysis of the variance was made for each shade, comparing the initial mean transmission of the guide with the mean transmission after little, moderate, and heavy use. The observed effect was found to be a decrease in over-all mean transmission after use as compared to the initial mean transmission, independent of the amount of use. The standard deviation before use ranged from 0.4% to 0.75% of the average transmission values, while the standard deviation after use ranged from 0.4% to 2.5% of the average transmission value for any one shade. This increase with use was to be anticipated as a result of variations in handling.

Results

Two factors determined from the analysis were: *(1)* the amount of usage (little, moderate, or heavy) did not significantly influence variation in transmission of the guide during the period of use, and *(2)* the reduction in transmission values after four months of field use was within a maximum of 2.2% of the average transmission value for any one shade.

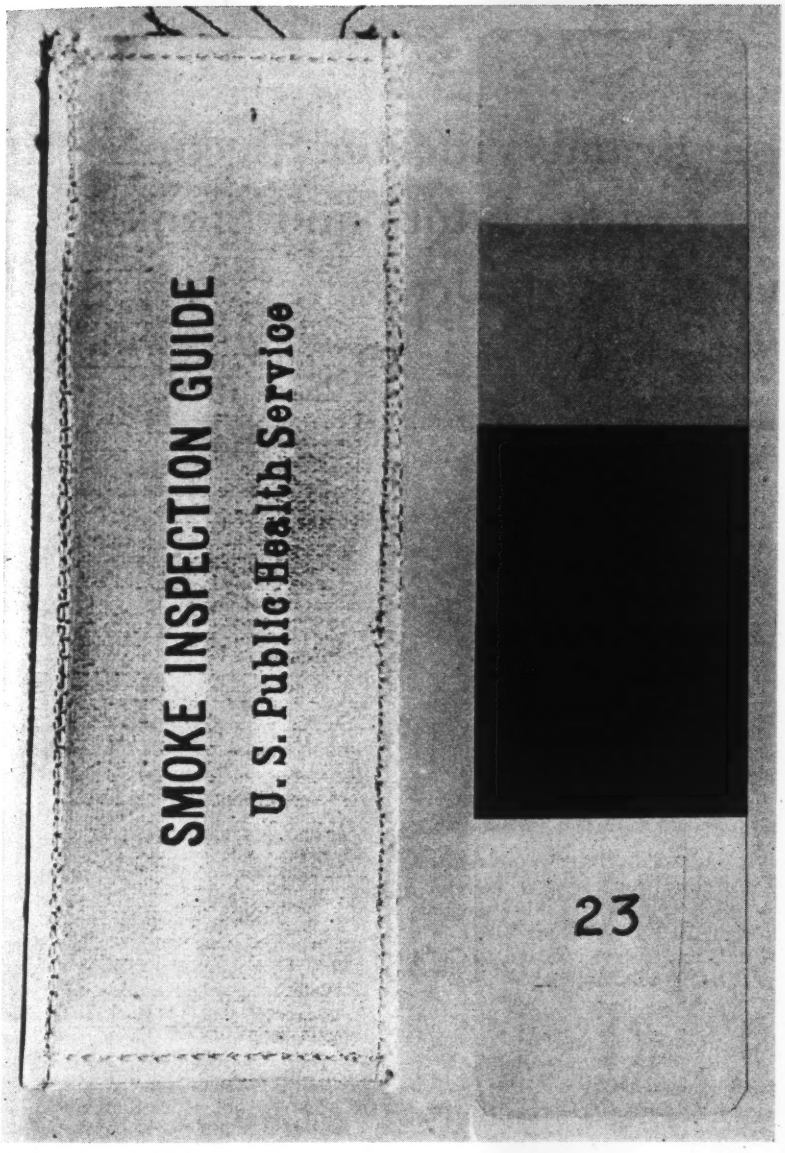

Fig. 3

Since this reduction in transmission is apparently a function of aging and not of use, an anticipated effective life for the guide, based on a specific percent reduction in transmission, can be predicted by extrapolation. Assuming a straight-line function, which probably is a more stringent extrapolation than actually exists, a predicted life of one year would have a reduction in any one shade within 6.6% of the average transmission value. Although a re-evaluation of the aging function of the guides will be made to confirm this prediction, present indications are that new calibrated guides will have a life expectancy of one year.

Use of the guide as a result of field application was evaluated on three bases: *(1)* interferences, *(2)* ease of application, *(3)* maintenance.

Interferences affecting the application of the guide include light reflection, background objects, and wind. Degrees of interferences were classified as negligible, small, moderate, and large. Results *(Table II)* show that 80% of the observers found negligible interferences with reading and only 16% rated interference as moderate to large. More than half of the 16% were from one agency in which personnel indicated pre-existing bias against the film-guide technique.

In evaluating the ease of application of the guide, the three factors considered were arrangement of the shades, durability of the guide, and training required for its use. These factors were classified as satisfactory or unsatisfactory. Eighty-one percent of the observers found these factors satisfactory.

Maintenance was concerned only with the problem of keeping the guide clean and usable. One hundred percent of the observers rated the guide satisfactory in this respect.

Several suggestions for improvement resulted from the interviews, including framing the guide, providing clear intervals between shades, providing larger shade areas, and changing the number of shades provided. These suggestions will be studied and may be incorporated, at least in part, in production models of the guide.

Conclusions

Field experience with the PHS Smoke Inspection Guide has confirmed our belief that it is a better, more reproducible device for smoke inspection than the printed Ringelmann Chart. Results permit specifications for production models which can be made available to such agencies and organizations as may wish to use them.

TABLE II

Smoke Guide Questionnaire Evaluation

	Negligible	Small	Moderate	Large
Interference Effects (3 parts)	40	2	6	2
	Satisfactory		Unsatisfactory	
Ease of Application (3 parts)	37		9	
Maintenance (1 part)	17		0	

The Use of the Von Brand Filtering Recorder in the Evaluation of Incinerators and Smoke Abatement Devices*

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The Bureau of Laboratory of the Department of Air Pollution Control, City of New York, is at present pursuing an active research and development program for the control and the abatement of pollution from incinerators and similar devices. Pollution from such sources is a serious problem in the City of New York.[1]

Customary chemical methods for evaluating incinerators and smoke abatement devices are complicated, tedious, and time consuming;[2,3,4] consequently an effort was made to develop and use physical and instrumental methods wherever feasible.

The analysis of flue gases in the field was found to be particularly cumbersome. In previous work we adapted the use of the Titrilog[5] to the study of incinerator flue gases, thus employing an instrumental means for evaluating flue gases. This method was found to be useful both in the laboratory and in the field.

Most governmental and other authorities base their acceptance or rejection of adequate incinerator operation and other combustion devices on the smoke or solids content of the effluent flue gases. A faster method of the evaluation of incinerator operation would be the development of an instrumental or physical method for giving virtually instantaneous readings and at the same time provide some sort of a permanent record. The instrument should be light enough to be portable and rugged enough to withstand field conditions.

*Contribution from Bureau of Laboratory, Department of Air Pollution Control Sept. 1957.

Methods for Testing Incinerators

In addition to the customary chemical methods for testing incinerators, there are a number of other methods in common use which are based on a visual response with and without mechanical aids and can be used for instantaneous results. A brief discussion of each of these methods follows:

(a) Ringelmann Chart

This chart was developed by Professor Ringelmann of Paris and is now widely used by law enforcement officers who have adopted standards based upon the chart.[6] It was first introduced into the United States in 1897 and is still being used to the present day. The Ringelmann system is based upon a scheme whereby graduated shades of gray, varying by five equal steps between white and black, may be accurately reproduced by means of a rectangular grill of black lines of definite width and spacing on a white background. The Bureau of Mines distributes a variation of this chart providing for four shades of gray varying between 20% and 80% black. The observer compares these shades against the smoke issuing from the stack and estimates the percentage of black as closely as he can.

It is not sensitive or versatile enough for our purpose. In addition, it does not give automatic readings or provide a permanent record.

(b) Bacharach True Spot Smoke Tester

In this method 2250 cubic inches of flue gas/in.^{2} of surface area are drawn through a filter paper by means of a hand pump. The grey spot is then compared against a chart divided into nine shades of grey. Vandaveer[7] used a Bacharach spot smoke tester to test the smoke from domestic gas-fired incinerators. This method was found in our laboratory to be somewhat better than visual inspection in that it permitted the elimination of many of the subjective factors inherent in the observer system. However, for a continuous picture of operation it required the taking of a great many samples. In addition, the Bacharach scale ranging from 1 to 9 does not provide sufficient graduations for our work.

(c) A.I.S.I. Automatic Smoke Filter[8, 9]

In this method, as in the Bacharach spot tester, the flue gas is drawn through a filter paper. However, this is done automatically by means of an air pump. The machine can be set to time the period of sampling. The smallest period, however, of our instruments was much too long for our

purpose. In addition, the spot formed gives an overall average for the time sampled but no picture of the incineration process itself. This instrument was primarily developed for atmospheric pollution work although it may be adapted for stack gases by diluting the flue gas sample with air.

(d) Von Brand Smoke Recorder[10, 11]

For our purpose, the Von Brand continuous portable smoke recorder adjusted for continuous rather than spot recording, was found to be preferable to the other devices. It gives automatically a fairly permanent picture of the process under study and completely eliminates the necessity for an observer's subjective judgment. It can also be used to evaluate a smoke abatement process for it is equipped to give a continuous picture of the character of the flue gases before and after the abatement device. When the double trace head is used, results lie side by side for easy and rapid comparisons. By adapting the "*Ruds System*"[12] to this method, the comparisons can be expressed on a numerical basis; and major observational and subjective errors can be eliminated.

The machine is small, easily portable, sturdy, can be set up in a few minutes, and will run with practically no supervision. By the use of various heads, velocities, and timing devices it can be adjusted to take care of a variety of needs and situations. Care must be taken, however, to avoid getting the tape wet for it may tear.

Operation and Characteristics of the Von Brand Recorder

(a) Operation

For this work an H 55188 H.D. portable continuous recording type of instrument was used. This instrument is provided with a vacuum pump which aspirates air, by means of a 1/12 H.P. motor, through a filter paper which is supplied as tape from a spool. The type of head used, the type of tape movement (continuous or intermittent spot) and the speed of the tape can be varied to fit the situation. The recording head is kept heated to prevent condensation of moisture and to condition the filter paper. The machine automatically marks off 1 in. intervals on the tape for timing purposes. Three interchangeable recording heads are available. The single trace heads can produce a trace of ¼ in. or ½ in. width. The dual head produces two ¼ in. traces while the triple head produces three 3/16 in. traces. For studying the smoke abatement devices, a head with a double inlet was used. A tape speed of 2 in./min. was found to be satisfactory and the smoke line traced on the filter paper was well within the readable range. A total of 0.07 ft.^{3} of air/min. was drawn through the filter paper. An oil manometer was attached between both inlets to make certain that the same quantity of air was drawn through each. Pinch clamps may be used to regulate the flow but were found to be unnecessary. It is advisable to permit the head to heat for 10 min. before starting the test.

(b) Probes

The probes used in these experiments consisted of ¼ in. flexible copper tubing. These probes were inserted into holes in the flue of an experimental incinerator. One probe was inserted below our experimental smoke abatement device and the other above it. No condensate traps were used since they were found to be unnecessary. Hunter[12] claimed that for optimum accuracy it is advisable to regulate the air flow so that the gas velocity in the probe is 2 or 3 times the velocity in the flue. The standard method is to sample isokinetically. For a minimum lag time the probes should be as short as possible but still long enough to permit some cooling of the hot gases. For testing incinerators in the field a single head inlet is used and the probe is inserted through the hopper door on the highest floor. It is advisable to keep the end of the probe as close to the center of the flue as possible. Masking tape may be used to close up the narrow opening left in the door because of the probe. If the incinerator has a settling chamber, the probes should be inserted in the flue above this chamber.

(c) Sensitivity

The sensitivity of this instrument is adjustable over a wide range simply by varying the tape speed or velocities of the sampled gas. At low tape speed cigarette smoke in a room leaves a visible brown stain while at high tape speed the blackest smoke can be measured. When used in conjunction with the RUDS system of evaluating the trace, the filter paper of the instrument can read smoke invisible to the naked eye.[12]

RUDS System of Evaluating the Smoke Stain

(a) Explanation of the term RUDS.

In obtaining optical density (Log $[I_O/I]$) light reflectance and transmission correlate very well and can therefore be used interchangeably. The optical density may then be multiplied by a constant K equal to 100 and the result called *Dirt Shade*. Therefore:

$$\text{Dirt Shade} = \text{Log}_{10} \frac{A}{B} \times 100$$

A = % Reflectance clean filter paper
B = % Reflectance soiled filter paper

For simplification the *% Reflectance clean filter paper* is set at 100 on the reflectance meter and therefore a *dirt shade* of 0 is *absolutely* clean while a dirt shade of 100 is *absolutely* black.

The dirt shade may then be divided by the amount of linear feet of air per minute passing through the filter paper and the result called the soiling index. This unit of soiling index is called "RUDS" (Reflectance Units of Dirt Shade). In ordinary air pollution work 10,000 linear feet of air are taken as the basic unit; however in incinerator work this may be too large and 1,000 linear feet of air/min. may be used if desired.

(b) Instrument for Measuring Reflectance

For our work we used a Photovolt Photoelectric Reflection Meter Model #610.[13] This consists of two units: the instrument proper which contains the indicating meter, the power supply, and the controls, and the search unit which contains the light source and the photocells. A green tristimulus filter is used for this type of work and is inserted into the search unit.

(c) Preparation of Filter Paper

After the smoke stain has been traced on the paper it is read directly by placing the search unit on it. When a dual head was used, our method was to fold the paper lengthwise in half. A channel which was just about the width of the folded filter paper was grooved into a block of wood. The search unit was centered over the groove and the filter paper drawn through it for readings. The instrument was calibrated to

read 100% when a clean filter paper was used.

Method

(a) Equipment

As an example of the use of this method and the RUDS system, the efficiency of a smoke abatement device placed in the flue of an experimental laboratory incinerator was determined. This incinerator was described in a previous paper.[5] The smoke abatement device is still in a development stage. The probes were inserted into the flue; one above and one below the device. They were then connected to the inlets of a dual head. Since the smoke abatement device permits outside air to enter the flue, it was necessary to make two runs; one with the device off (considered as a blank), and the other with the device in operation. An oil manometer was connected between the two probes to keep the flow in each equal.

(b) Procedure

The incinerator was filled with newspapers, wood, and rubbish. The head in the Von Brand Instrument was permitted to warm up and then the incinerator was ignited. Tracings were made with the abatement device off and then the complete procedure was repeated with the abatement device in operation (see Fig. 1). The tracings were then read as previously described using the reflection meter. Readings were made at every inch of the tape using the inch markings as guides.

(c) Calculations

The reflection meter readings were the following:

Abatement device off		Abatement device on	
above	below	above	below
59	56	86	76
49	43	70	62
73	67	80	71
64	50	67	54
60	50	65	46
66	57	70	55
69	56	71	62
63	53	79	70
76	76	81	71
64	60	78	67
		70	55
		68	52
		64	50
		57	38
		66	52

The averages for the runs were as follows:

Device off		Device on	
above	below	above	below
64.3	56.2	71.5	58.7

$$\text{Dirt Shade} = \text{Log}_{10}\frac{A}{B} \times 100$$

A = % Reflectance clean filter paper
B = % Reflectance soiled filter paper

Substituting in the above formula the average result for each we get:

Device off		Device on	
above	below	above	below
19.3	25	14.6	23

To calculate linear feet of air through filter paper we proceed as follows:

Volume of air pulled through each trace was set at 0.035 ft^3/min. The speed of the filter tape was set at two ins. a minute. The width of each trace is ¼ in. Therefore the area of each 2 ins. of trace equals 2 x ¼ in. or ½ $in.^2$ Divided by 144 $in.^2/ft.^2$ we get 0.0034 $ft.^2$

$$\text{Linear feet of air} = \frac{\text{average flow rate in ft}^3\text{/min.} \times \text{time in minutes}}{\text{area of spot in ft}^2}$$

$$\text{Linear feet of air} = \frac{.035\ ft^3/min \times 1\ min}{.0034\ ft^2} = 10.3\ ft.$$

$$\text{Soiling Index (RUDS)} = \frac{\text{Dirt Shade}}{\text{Linear feet}} \times 10{,}000 = \text{RUDS/10,000 linear feet of air}$$

Substituting the above dirt shade values in this formula we obtain:

Smoke abatement device off — Above 1,840 RUDS/10,000 linear feet/air
Smoke abatement device off — Below 2,427 RUDS/10,000 linear feet/air
Device on — Above 1,417 RUDS/10,000 linear feet/air
Device on — Below 2,233 RUDS/10,000 linear feet/air

The difference with the abatement device off is 587 RUDS per 10,000 linear feet of air. The difference with the device in operation is 816 RUDS per 10,000 linear feet of air. Therefore the decrease in smoke emission due to the abatement device is 229 RUDS.

Discussion

Reflectance and weight of dust as such have no relation to each other. Actually reflectance gives a better

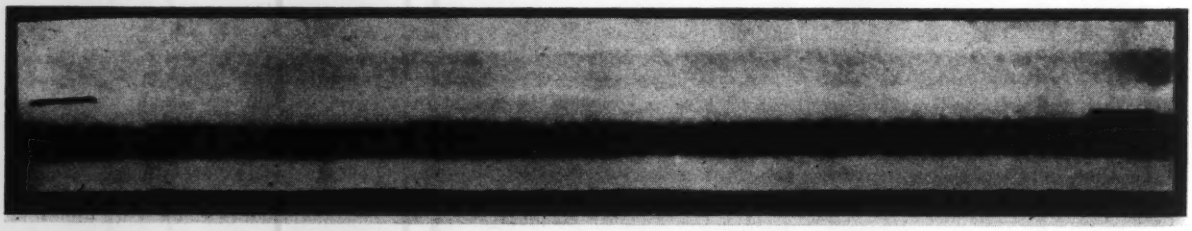

Fig. 1. Von Brand filtering recorder dual trace.

picture of the nuisance value of incinerator smoke than the weight of the individual particles. A large particle carried up the flue will have very little effect on the RUDS but will greatly increase weight determinations. Yet this particle will not travel far or be a significant nuisance. Reflectance is a measure of the surface area of the smoke and solid matter. The finer the particles, the further they will travel and the longer they will remain suspended in air. We are most interested in particles of 3μ or less and these are the particles which affect reflectance readings to the greatest extent.

Summary

This paper describes a method for evaluating incinerators and smoke abatement devices. It describes other methods used and discusses the reasons why they are not useful for this purpose. It is to be noted that this instrument cannot be used to give a weight of total particulate matter but rather a comparative measurement of the quality or density of the smoke. When used in conjunction with the Titrilog, it gives a good indication of the health and nuisance hazard of the incinerator under test.

References

(1) Leo P. Flood. Solving the Problem of Flue Fed Incinerators. *Air Pollution Control Assoc.* 50th Annual Meeting, St. Louis, June 1957.

(2) Carl V. Kanter, R. G. Lunche, and A. P. Fudurich. Incinerator Testing and Test Results. *Air Pollution Control Assoc.* 49th Annual Meeting, Buffalo, May 1956.

(3) J. E. Yocum, C. M. Hein, and H. W. Nelson. *J. Air Pollution Control Assoc.*, **6**, No. 2, 84 (1956).

(4) F. R. Rehm. Incinerator Testing and Test Results. *Air Pollution Control Assoc.* 49th Annual Meeting, Buffalo, May 1956.

(5) I. Ettinger, M. Braverman, and M. B. Jacobs. The Use of the Titrilog in the Study of Incinerator Flue Gases. Dept. Air Pollution Control, City of New York, In process (1957).

(6) R. Kudlich. Ringelmann Smoke Chart. *U.S. Bureau Mines, Inform. Circ. 7718* (Aug. 1955).

(7) F. E. Vandaveer. *J. Air Pollution Control Assoc.*, **6**, No. 2, 90 (1956).

(8) W. C. L. Hemeon. Instruments for Automatic Pollution Measurements. *Proc. Air Pollution and Smoke Prevention Assoc. Amer.* pp. 115-123 (1951).

(9) W. C. L. Hemeon, G. F. Haines, and H. M. Ide. *Air Repair*, **3**, 22 (Aug. 1953).

(10) E. K. Von Brand. *Mech. Eng.*, **72**, 479 (June 1950).

(11) C. W. Gruber and E. L. Alpaugh. *Air Repair*, **4**, 143 (Nov. 1954).

(12) H. C. Hunter. Diesel Smoke Measurement, SAE Golden Anniversary Diesel Fuel Meeting, St. Louis, (Nov. 1955).

(13) E. Alpaugh. *Air Repair*, **2**, 21 (Nov. 1952).

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Nitric Oxide and Nitrogen Dioxide in the Los Angeles Atmosphere*

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Numerous studies have now confirmed that nitrogen oxides and organic matter enter into photochemical reactions to form an unpleasant atmospheric mixture in Los Angeles which is called "smog." Since oxides of nitrogen are formed during combustion both from the burning of organic nitrogen compounds and from the combination of atmospheric nitrogen and oxygen at elevated temperatures, the determination of the concentration and distribution of atmospheric oxides of nitrogen becomes important from an air pollution standpoint.

Previous measurements of the atmospheric concentrations of nitrogen oxides in Los Angeles have been made on an intermittent basis.[2,5,9] McKee[6] reported on atmospheric nitrogen dioxide measurements in Houston, Texas, and Moore, *et.al.*[8] measured nitrogen dioxide in the atmosphere in Windsor, Ontario. All of these measurements were made on an intermittent basis.

Cholak *et.al.*[1] reported on nitrogen dioxide measurements in Cincinnati, Ohio with a continuous recorder. Recent measurements by the Los Angeles County Air Pollution Control District with continuous recorders have been summarized.[4] Other references and a summary have been published by Miller.[7]

Late in 1954 it was decided, due to the dynamic character of the reactions in Los Angeles smog, that continuous recording instruments were needed for measuring nitric oxide and nitrogen dioxide both for atmospheric measurements as well as photochemical studies. The results of this work resulted in a continuous recording instrument, which was described by Thomas, *et.al.*[13] Several models of this instrument have been built, including one which measured four atmospheric variables and recorded the result on a single strip chart recorder. The variables measured by this four-channel instrument were nitric oxide, nitrogen dioxide, oxidant, and oxidant precursor.

The four-channel instrument was used to monitor the atmosphere during the period September-November, 1955 at the California Institute of Technology in Pasadena, California. It was again used to measure nitric oxide and nitrogen dioxide in the atmosphere (a separate instrument was used for oxidant) at the Stanford Research Institute at 820 Mission Street in South Pasadena during the period October-November, 1956.

This work was undertaken with the objective of trying to understand the inter-relationships between nitric oxide, nitrogen dioxide, oxidant, and oxidant precursor. It has partially succeeded in this objective, but much of the atmospheric chemistry is still obscure.

The instrument included a four-channel Brown strip chart recorder which made successive readings on a special 7-cell colorimeter. The colorimeter provided a means of measuring the reaction from four absorbing columns, one for each of the atmospheric components mentioned above. Nitrogen dioxide was measured after contacting the air with modified Griess reagent; nitric oxide plus nitrogen dioxide was measured by first converting nitric oxide to nitrogen dioxide with a carefully controlled concentration of ozone, and measuring the total nitrogen dioxide with modified Griess reagent; oxidant was measured with 20% neutral potassium iodide; oxidant precursor was measured by first passing the air sample through a 50 *l.* Pyrex flask irradiated with four mercury arc lights, and then into a contacting column containing 20% neutral potassium iodide.

There were several interruptions due to mechanical failures in 1955, which were inherent in a developmental instrument. Nevertheless, sufficient data were accumulated in a two-month period to show some definite patterns. In 1956, the instrument was rebuilt, most of the mechanical problems solved, and scattered data for a two-month period were obtained. The location of the instrument in 1956 was about two miles from that used in 1955, and was a few hundred yards from the Pasadena freeway.

Summary of Data Obtained in 1955 and 1956

Monthly hourly averages of oxidant and oxidant precursor for the three-month period of September, October, and November 1955 appear in Fig. 1; the average nitric oxide and nitrogen dioxide for October-November, 1955 are shown in Fig. 2. Similar curves for oxidant, nitric oxide, and nitrogen dioxide for the two-month period of October and November, 1956 are given in Fig. 3.

Data for one day, November 23, 1956 for nitric oxide, nitrogen dioxide, and oxidant are shown in Fig. 4. On this day, a surface inversion was reported in Santa Monica by the Weather Bureau at the time all four

*Presented at the 132nd National Meeting, American Chemical Society, New York, N. Y., Sept. 8-13, 1957.

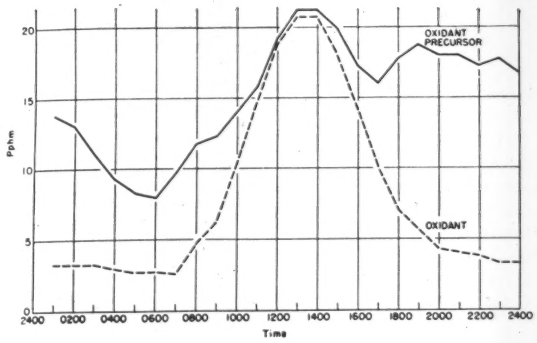


Fig. 1. Average Concentrations of Oxidant and Oxidant Precursor. Pasadena, September-November 1955.

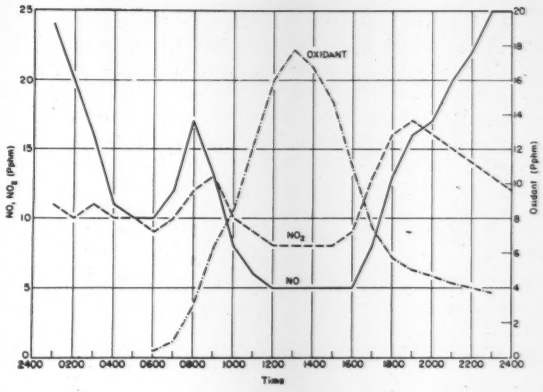


Fig. 3. Average Concentrations of Oxidant, Nitric Oxide, and Nitrogen Dioxide. South Pasadena, October-November 1956

soundings were made (0100, 0700, 1300, 1900 PST).

Data for another day of interest, November 6, 1956 are shown in Fig. 5, in which the total nitrogen oxides (nitric oxide plus nitrogen dioxide measured by the modified Griess reagent recorder) are compared with data obtained by the Franklin Institute long path infrared cell located about 100 ft. from the colorimetric recorder. The Franklin Institute data were obtained by taking an atmospheric sample into the infrared cell, adding an excess of ozone to convert nitric oxide and nitrogen dioxide to nitrogen pentoxide, and measuring its concentration in the infrared at 8 μ relative to a calibration curve prepared with nitrogen dioxide treated in the same manner.[11] The Weather Bureau reported a surface inversion on November 6 at Santa Monica at 0700 and 1900 PST, with the inversion base at 1230 PST at an altitude of 689 ft.

Discussion

Average oxidant precursor shows a greater value than oxidant both day and night, as shown in Fig. 1, although the maximum is about the same for both components in the middle of the day. Oxidant precursor is distinctly greater during the hours when the sun's intensity diminishes, and at night. A minimum was observed at 5 to 6 A.M. The average oxidant-forming power of the atmosphere, as measured here by the oxidant precursor values, averaged more than 15 pphm. in the evening hours and, at its minimum at about 6 A.M., averaged about 8 pphm.

Nitric oxide was found to occur at larger concentrations than nitrogen dioxide during the night, but a reversal occurred during the daylight hours as shown in Figs. 2-5. Moreover, there were two maxima for both components at about 8 A.M. and again about 6 to 10 P.M., with two minima: One in the middle of the day at about 11 A.M. to 2 P.M. and in the early morning at about 4 to 6 A.M. The minimum observed in the middle of the day occurred at the same time as the maximum oxidant value measured. The rough parallelism between nitric oxide and nitrogen dioxide concentrations at night suggests that nitrogen dioxide is being formed from nitric oxide, presumably by the reaction $2NO + O_2 \longrightarrow 2NO_2$.

On comparing Fig. 2 with Fig. 3 it is seen that the average values for 1956 were greater than the values for 1955. Although the instrument had been reconditioned and recalibrated between the two periods of measurement, the effects of these changes are thought to be less important than the relocation of the instrument from California Institute of Technology in Pasadena to Stanford Research Institute at 820 Mission Street in South Pasadena, about two miles away. The South Pasadena location is a few hundred yards from the Pasadena freeway, which is used at that point by about

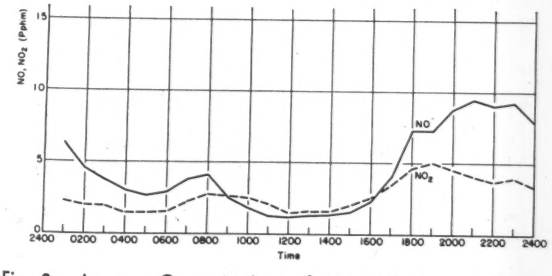


Fig. 2. Average Concentrations of Nitric Oxide and Nitrogen Dioxide. Pasadena, October-November 1955.

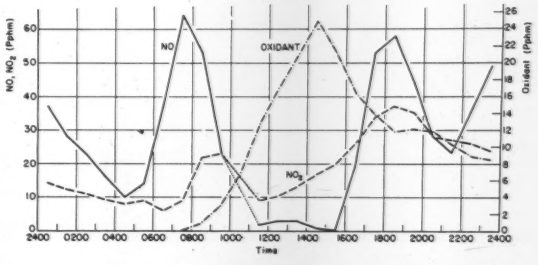


Figure 4. Oxidant, Nitric Oxide, and Nitrogen Concentrations. South Pasadena, November 23, 1956

35,000 vehicles per day. The number of vehicles passing California Institute of Technology is much less. Since automobile exhaust is one of the major sources of nitrogen oxides, it seems reasonable to assume that this difference in observed concentration is largely due to the proximity of the 1956 sampling point to a major traffic artery.

The effects of surface inversions on the nitrogen oxides concentration is seen in Figs. 4 and 5. On these days, total nitrogen oxide concentration of about 70 and 90 pphm. were observed in the early morning. This concentration is thought to be a result of the close proximity to the freeway with lateral transport of the nitrogen oxides from motor vehicle exhaust to the sampling station. The cause of the rapid disappearance of nitrogen oxides is discussed below.

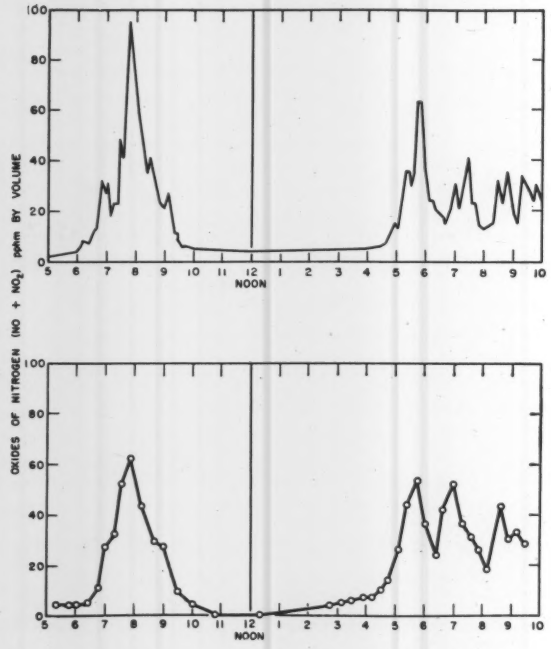
The curves in Fig. 5 are shown to compare the results obtained with an infrared procedure with those from the chemical nitrogen oxides recorder. The Franklin Institute data as measured by infrared absorption paralleled the chemical colorimetric measurement from 6 A.M. to 6 P.M. However, considerable fluctuations were found between 6 and 10 P.M. by both methods of measurement, and the agreement was less satisfactory in the evening hours. It is postulated that this lack of agreement was due to parcels of contaminated air slowly passing over the respective sampling points, and that the differences between the two methods of measurement were due to the 50-ft. difference in height between the two sampling points. If this explanation is correct, the importance of locating sampling points for comparative studies at very close proximities to each other is again emphasized.

An interesting relationship resulted when the numerical values of hourly oxidant were subtracted from the corresponding oxidant precursor value, and these, together with the total nitric oxide plus nitrogen dioxide values, were plotted against each other. The results of such a plot are shown for October, 1955 in Fig. 6. The close parallelism of these two curves suggested the preparation of a plot of these two values. This appears in Fig. 7 with the values of oxidant precursor minus oxidant plotted as ordinates against total nitrogen oxides as abscissa, together with a straight line fitted by the least squares procedure. These data support the argument by Littman, *et al.*[3] that nitrogen oxides are the major contributor to oxidant precursor.

A comparison of the 1955 and 1956 data with those reported in 1954[1] is of interest. The average values obtained in Pasadena in 1954 on an intermittent basis at the same location as that used in the 1955 study varied from 15 to 25 pphm. between 6 and 8 A.M., using a different method of sampling and analysis. In 1955, the average values of total nitric oxide plus nitrogen dioxide at these hours was 4 to 7 pphm. This difference is thought to be in large part due to the difference in method of analysis. The 1954 data reported a minimum at 6 A.M. and a maximum at 8 A.M., similar to those found in 1955. The continuous recorder gave much more complete records and also showed that larger concentrations exist at night than during the daylight hours.

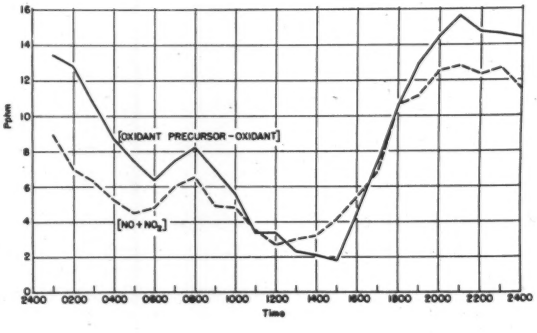
As an indication of the contribution of motor vehicle traffic to the nitrogen oxides concentration the traffic count on the Pasadena Freeway for July 16, 1956 is shown in Fig. 8. The location of the traffic counter was about one mile from the sampling station, but since there are few exits or entrances to the freeway between the two points, the traffic count shown is considered to be fairly representative of the actual count closer to the sampling station.

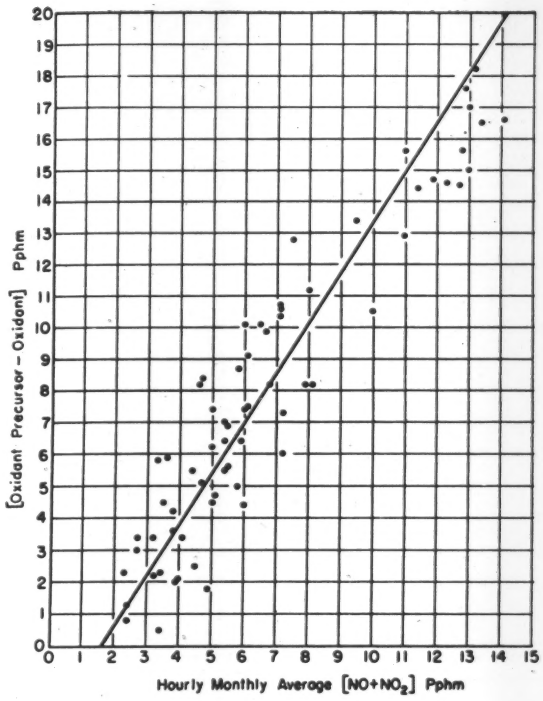
The two major traffic surges at about 0730 and 1730 in Fig. 8 are seen to correspond roughly to two peak concentrations of nitric oxide

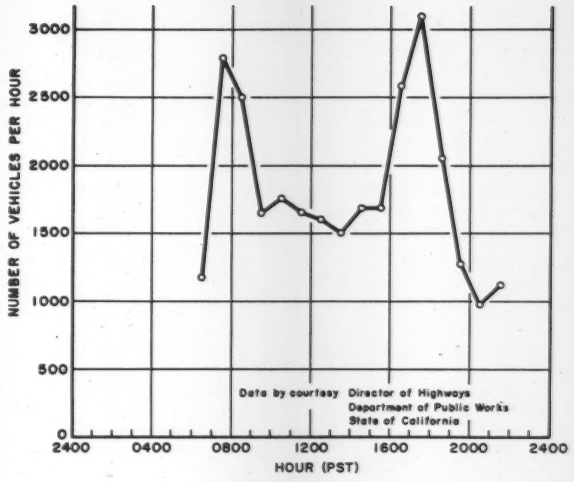


(Left) Fig. 5. Concentrations of Total Oxides of Nitrogen by Chemical Procedure (upper curve) and Infrared Procedure (lower curve). South Pasadena, November 6, 1956.

(Below) Fig. 6. Average Values of (Oxidant Precursor Minus Oxidant) and (Nitric Oxide Plus Nitrogen Dioxide). Pasadena, October 1955.






NUMBER OF VEHICLES PER HOUR
HOUR (PST)
Data by courtesy Director of Highways
Department of Public Works
State of California

(Above) Fig. 8. Hourly Traffic Count. Pasadena Freeway, July 16, 1956.

(Left) Fig. 7. Average Values of (Oxidant Precursor Minus Oxidant) vs. (Nitric Oxide Plus Nitrogen Dioxide). Pasadena, September-November, 1955.

shown in Figs. 3 and 5. However, the much lower measured concentrations during the middle of the day when the traffic count is about one-half that observed during the rush hours must be explained by some other mechanism, involving meteorological factors and chemical reaction.

Interpretation of Observed Curves

The data reported above are the resultant of the interaction of the following variables: *(1)* rate and quantity of emission of nitrogen oxides, largely from automobiles; *(2)* meteorological factors including inversions and winds; and *(3)* thermal and photochemical reactions. All of these are not readily measured or completely understood and a quantitative explanation of the relations is not possible. A qualitative discussion is given below.

The rise in nitric oxide concentration in the early morning may be explained by greatly increased vehicular traffic. Nitric oxide at these concentrations is slowly converted to nitrogen dioxide by the thermal reaction *(1)*:

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \quad (1)$$

The rate of this reaction, however, is relatively slow, and at a concentration of 1 ppm. of nitric oxide in air, its half life has been calculated to be 100 hr. Nevertheless, a small amount of nitrogen dioxide is formed. At sunrise, photochemical reactions are initiated and the reactions represented by equation *(2)* followed by *(3)* can be expected.

$$NO_2 + h\nu \longrightarrow NO + O \quad (2)$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (3)$$

However, presence of even a small concentration of ozone makes probable the fast reaction represented by equation *(4)*:

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (4)$$

Such a chain of reactions has been frequently suggested, and the difficulty of explaining the subsequent smog effects has been pointed out. Three difficulties are apparent: *(1)* the concentrations of both nitric oxide and nitrogen dioxide diminish to relatively small values by about 9 or 10 A.M., indicating either rapid dissipation or further reaction; *(2)* one of the principal sources of ozone in smog is thought to be the photolysis of nitrogen dioxide, but the peak value of ozone (assuming all the oxidant observed is ozone) is observed some four hours after the peak value of nitrogen dioxide is measured — in other words, the nitrogen oxide values are at a minimum when the ozone is at a maximum; and *(3)* there is a disagreement between the estimated rate of formation of ozone, the estimated rate of its reaction with nitric oxide, and the measured concentrations of nitrogen dioxide, nitric oxide, and oxidant.

The decrease in nitrogen oxides in the middle of the day appears to be due to either of two effects. One of these is meteorological, such as a breaking of the inversion. The other is a thermal reaction, probably with organic matter. One such reaction has been identified by the Franklin Institute workers,[11,12] who have found a peroxyacyl nitrite, RC(:O)OONO, both in the Los Angeles atmosphere, and in laboratory photochemical studies with nitrogen dioxide and hydrocarbons. This compound should hydrolyze in aqueous solutions and give nitrite ion which would be measured by the nitrogen dioxide instrument. Doubtless, part of the reported nitrogen dioxide during the middle of the day is due to this. In any event, improved methods of measurement and further studies of the reactions are

necessary before a complete understanding is reached.

Nothing that has been said above is to imply that work on methods of diminishing both organic matter (hydrocarbons and derivatives) and nitrogen oxide emissions should be deferred. The Air Pollution Foundation is proceeding on the assumption that reduction of these materials is necessary and desirable, and is pursuing methods for accomplishing this.

Summary

Nitrogen oxides are emitted from motor vehicle exhaust, chimneys, stacks, and other combustion processes. Part of the daily variation reported here is due to variance in the rate of emission from these sources, primarily as a result of the location of the sampling point near a heavily travelled freeway. Other major factors contributing to the observed variation are wind speeds and direction; height of the inversion layer; the thermal reactions of nitric oxide with oxygen, ozone and organic materials; and the photochemical and thermal reactions of nitrogen dioxide with ozone, sunlight, and organic materials.

Acknowledgments

Thanks are due to George Doyle of Stanford Research Institute and Edward M. Liston of the Air Pollution Foundation for operating the chemical recorders; to Philip L. Hanst and Edgar R. Stephens of Franklin Institute for the infrared data; and to A. L. Himelhoch of the California Division of Highways for the traffic counts.

References

(1) Jacob Cholak, Lawrence J. Schafer, David Yeager, and W. J. Younker, *A.M.A. Arch. Ind. Health.* **15,** 198-206 (1957).

(2) G. P. Larson, J. R. Taylor, and W. J. Hamming, *Proc. 3rd Nat. Air Pollution Symposium, Pasadena, California.* 1955. pp. 33-42.

(3) Fred E. Littman, H. W. Ford, and N. Endow, *Ind. Eng. Chem.*, **48,** 1492-98 (1956).

(4) Los Angeles County Air Pollution Control District, Automatic Instrument Operation and Manual Air Sampling. January 29, 1957.

(5) Paul L. Magill, *Proc. 1st Nat. Air Pollution Symposium, Pasadena, California,* 1949, pp. 61-68.

(6) Herbert C. McKee and B. W. Beadle, Air Pollution Survey of the Houston Area. Technical Report No. 3, Southwest Research Institute, March 19, 1957.

(7) Lewis E. Miller, The Chemistry and Vertical Distribution of the Oxides of Nitrogen in the Atmosphere. Geophysic Research Paper No. 39, Air Force Cambridge Research Center, November 1954.

(8) G. E. Moore, A. F. W. Cole, and Morris Katz. *Proc. Air Pollution Control Assoc.*, 49th Meeting, 1956. Paper No. 24.

(9) N. A. Renzetti, *ed.*, An Aerometric Survey of the Los Angeles Basin August-November, 1954. *Air Pollution Foundation* (Los Angeles) Rept., **2,** No. 9, 139-65 (1955).

(10) *ibid.*, p. 147.

(11) W. E. Scott, E. R. Stephens, P. L. Hanst, and R. C. Doerr, Division of Refining, 22nd Midyear Meeting, American Petroleum Institute, Philadelphia, Pa., 1957.

(12) E. R. Stephens, W. E. Scott, P. L. Hanst, and R. C. Doerr, Division of Refining, 21st Midyear Meeting, American Petroleum Institute, Montreal, Que. Canada, 1956.

(13) M. D. Thomas, J. A. MacLeod, R. C. Robbins, R. C. Goettelman, R. W. Eldridge, and L. H. Rogers. *Anal. Chem.*, **28,** 1810-16 (1956).

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Evaluation of the Hazards of Ozone and Oxides of Nitrogen--Factors Modifying Acute Toxicity*†

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Occupational Health Program
Public Health Service
U. S. Department of Health,
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Ozone has been established without question to be a component of Los Angeles smog[1,2]. As an egent of distress and potential disease, ozone has been well documented[3]. Whether ozone, *per se*, is capable of becoming a health hazard in urban atmospheres is less certain, however. New information derived from animal experimentation on ozone atmospheres and nitrogen oxide-ozone atmospheres under varying conditions is presented here in the hope that it will permit a more exact evaluation of the potential hazards to urban and working populations exposed to ozone. This becomes especially important in the light of the recent report of Kleinfeld[4] on ozone injury of the lungs among welders using the new inert-gas shielded arc process. These represent the first instances of human injury from ozone ever to be reported.

Lethal Doses

Ample evidence has been presented[3], and in what follows, to show that ozone in acute exposures is a highly toxic and lethal substance. The LD50 values[a] for 3 rodent species, are given in Table I. It is seen that the susceptibility or natural tolerance, varies considerably with the species, the hamster being the least susceptible of the species tested. Although insufficient numbers of other species have been exposed to ozone to determine accurate LD_{50} values, the dog would appear to resemble the hamster in natural tolerance to ozone on the basis of the evidence at hand; the rabbit has a tolerance between that of the rat and the hamster.

Comparison of the LD_{50} values for ozone with those for the industrially well known and highly toxic gas, phosphine, shows an LD_{50} value for phosphine[6] of 60 ppm. for the rat under similar conditions of exposure, indicating ozone to be approximately 12 times more toxic in single acute doses. The high toxicity of ozone is all the more remarkable when it is noted that but one-quarter of the inhaled ozone reaches the lungs[7], where it produces pulmonary edema, hemorrhage and eventual death. Taking this into account, the absolute amount of ozone killing the rat is but 0.025 ml. pure ozone gas at standard temperature and pressure, or 50 μg.; a similar value for the mouse is 4 μg. of ozone. This assumes a respiratory minute volume[b] of 100 ml. for the rat and 10 ml. for the mouse. The order of 1000 μg. of phosphine is required to kill the rat, assuming in this case than 50% of the inhaled gas reaches the lungs. These figures provide striking evidence of the highly lethal character of ozone.

In all experiments reported here ozone was determined by the alkaline potassium iodide method of Smith and Diamond[8] as modified by Byers, Saltzman and Hyslop[9]. The total oxides of nitrogen were determined by the well known phenol disulfonic acid method: nitrogen dioxide by the specific method of Saltzman[10]. The accuracy of the ozone method is still under experimental scrutiny. It is possible that some factorial upward revision of the ozone values reported here may have to be made at a future date. A correction factor of approximately 1.5 appears probable at this date. The method, however, was the best available at the time these experiments were performed.

(a) The LD50 value is the dose of a substance that will on the average kill 50% of a significant number of animals exposed under specified conditions. Several experimentally simple and statistically sound methods of obtaining LD50 values are available; the one used in this work is that of Weil[5].

(b) The respiratory minute volume is the volume of air inspired during 1 min. by an animal while at rest.

TABLE I

Acute Ozone Toxicity

Lethal Doses for Small Animals

Ozone Concentration. ppm. by vol. Duration of Exposure. 4 hrs.

Animal Species	Av. Body Wt. g.	Ozone LD_{50}[a] ppm. by vol.	Range[a] ppm. by vol.
Mouse, albino, male	22	3.8	3.6-4.1
Rat, albino, male	250	4.8	3.6-6.4
Hamster (Cricetus auratus,) male	75	10.5	9.1-12.1

(a) Determined according to method of Weil[5].

*Reprinted from the *A.M.A. Arch. Ind. Health* (March, 1957) **15**, 181-190. Copyright 1957, by the American Medical Association.

†Presented at the International Ozone Conference, Nov. 30, 1956, Chicago, Illinois.

Toxicity of Ozone Prepared from Air and Oxygen

Because of the possibility that ozone prepared by electric discharge from laboratory, oil-compressed air might have toxic qualities different from that prepared from oxygen, a series of toxicity tests in mice were made at varying concentrations of ozone and periods of exposure utilizing the 4 possible combinations of air, oxygen and air cleaned by scrubbing with chromic acid and sodium hydroxide. The results are shown in Table II. It is seen that no conspicuous difference in toxicity to mice occurred from any of the different means of preparation of ozone when tested at concentrations between 4 and 10 ppm.; if any tendency was evident, the ozone prepared from oxygen and scrubbed diluting air was slightly less toxic than that from air and diluted with unwashed air.

Effect of Concentration and Time

A study was made in mice to determine whether ozone obeyed the toxicologic rule that the product of the concentration and time of exposure produced a constant, toxologic response, CT = K, over a concentration range of from 1-50 ppm. If a positive correlation is found, such information permits interpolation and extrapolation of the variables of exposure without the labor of experimental determination. A plot of the values in Table II from 2.5-50 ppm. ozone show reasonably good linearity, with the exception of the single response to 4 ppm. ozone prepared from air. When the entire experience of the other 3 tests at this level were used, however, close agreement to linearity was found. No fatal response to quiescent exposure to ozone at 1 ppm. was observed, no matter what the duration (cf Table VII).

Negative Role of Nitrogen Oxides in Ozone Toxicity

There is an erroneous impression, unfortunately widespread, gained from the misinterpretation of certain studies[12,13] that *the contamination of ozone with oxides of nitrogen has been partly responsible for the observed toxicity and that ozone is not nearly so toxic as it has been thought to be.*[c] There are at least two reasons for this misimpression: *1.* The reported animal toxicity data were insufficient to permit the conclusion that nitrogen oxides associated with ozone production contributed to the over-all toxicity. *2.* The reported experiments dealt with abnormally high concentrations of nitrogen oxides (approximately 50% of the ozone concentration). In all ordinary methods of ozone production by electric discharge the amounts of nitrogen oxides are relatively insignificant[11]. The evidence surrounding this question, presented in[3] weighed heavily against the conclusion that nitrogen oxides contributed significantly to the toxicity of ozone, but left the matter open to further experimentation. The question was finally resolved to our satisfaction in further experiments in which mice were subjected to various mixtures of ozone and oxides of nitrogen, and the resultant toxicity compared with that from ozone alone. This is shown in Table III. It may be seen that although a uniformly increasing degree of mortality in mice is observed with an increasing concentration of ozone alone, no such increase was demonstrated in mice exposed to increasing concentrations of nitrogen oxides mixed with ozone. Not until the total concentration of irritant gases far exceeded the LD_{50} for ozone alone (*i.e.* 4 ppm.) were comparable lethel effects produced by the mixture (*i.e.* 10 ppm. of nitrogen oxides and 4 ppm. ozone). Other experiments similar to these have been performed on several occasions with similar results. Thus it may be said that, contrary to past assertions, no evidence was found for ascribing the toxic effects of ozone to nitrogen oxides.

Indeed we know of no basis for such a view if one considers the toxicity of the individual nitrogen oxides in relation to that of ozone. The experimental evidence is the following: *1.* Pure ozone, prepared from pure tank oxygen and mixed with air purified by careful scrubbing is of itself highly toxic as has just been shown. *2.* The lower nitrogen oxides, N_2O and NO, are not significantly toxic nor would they be likely contaminants in ozone - generating sources. *3.* NO_2 has an LD_{50} value for rats of 65 to 75 ppm. for a 4-hr. exposure[15], a toxicity of a lower order of magnitude than ozone. *4.* Nitrogen pentoxide, the reaction product of NO and NO_2 in the presence of ozone is far less toxic than ozone as shown by the low toxicity given in Table III following exposures of animals to mixtures of NO_2 and ozone. Moreover, preliminary toxicity measurements of relatively pure solid N_2O_5 made by the action of ozone on P_2O_5-dehydrated, fuming nitric acid showed no deaths occurred upon exposures of at least 42 ppm. N_2O_5. This N_2O_5 preparation contained at the time of the exposure tests a maximum of 30 ppm. of NO_2 (presumably due to the spontaneous decomposition in the animal-exposure atmosphere), according to the new and sensitive method of Saltzman[10]. In the opinion of the present writer, the claims Diggle and Gage[16] make for the high toxicity of N_2O_5 are not supported by their reported data. *5.* Nitric acid vapor requires concen-

(c) Quoted from *Aviation Toxicology*, aeromedical Association, 971. The Blakiston Company, N. Y. (1953).

TABLE II

Mortality of Mice Following Exposure To Ozone At Varying Concentrations and Times and Prepared By Different Means.

Ozone Conc'n ppm.	Exposure Conc'n X Time CT Value pp. hrs.	Ozone From Air Diluted With		Ozone From Oxygen Diluted With	
		Unwashed Air	Washed Air or Oxygen	Unwashed Air	Washed Air
1	15	0/10[b]			
1	1200[a]	0/25			
2.5	6	0/5			
	10	3/10			
	37	4/5			
4	16	6/10	2/10	5/10	2/20
6	24	12/20		8/10	
8	48	10/10			
10	20	5/10	6/10	5/10	4/10
10	72	10/10			
24	72	10/10			
50	25			10/20	

(a) Discontinue exposure for 6 hrs. daily, 5 days week.

(b) Numerator refers to number of animals that died; denominator, to the number of animals exposed.

TABLE III

Mortality of Mice Following Single Exposures To Ozone and Ozone-Nitrogen Oxide Mixtures

Denominator: Number of Animals Exposed
Numerator: Number of Animals Dead.

Total Nitrogen Oxides Conc'n.	Ozone Concentration, ppm. by Vol.					
	<0.5	1	2.5	4	6	8
ppm. by vol. <0.2		0/10	3/10	6/10	7/10	20/20[d]
1-2				5/10		
4-5				2/10		10/10
10				8/10		
17[a]	0/10					
35[b]	0/10					
500[c]	2/6 (rats)					

(a) Containing 4 ppm. NO_2
(b) Containing 5.5 ppm. NO_2
(c) Nitric acid vapor containing 65 ppm. NO_2, -6-hr. exposure
(d) Mortality of other species at this ozone concentration: Rat, 6/6; Rabbit, 2/3, Dog, 0/1.

trations around 500 ppm to produce lethal effects in small animals as shown in Table III.

The entire question of nitrogen oxide impurities associated with the generation of ozone by electric discharge in air has been discussed by Saltzman, Byers and Hyslop.[11] Maximal amounts of nitrogen oxide impurities were 8.5% of the ozone generated, but less than 5% was the rule under normal operating conditions of a typical commercial ozone generator whose output was studied in detail. Barring the possibility of the presence of some unknown factor of extremely high toxicity such as free radical NO_3 that might form in greater quantities than found in these experiments under special or unusual conditions, there appear to be no reasonable grounds for the claims that nitrogen oxides contribute significantly to the toxicity of ozone electrically generated in present-day devices.

Irritation and Odor Levels

It is characteristic of the physiologic action of ozone to cause discomforting reactions in man other than the severely acute responses mentioned above for animals. It is common among individuals to experience headache and dryness of the throat, respiratory passages and eyes upon continued exposure to concentrations above 0.1 ppm. For this reason as well as others mentioned below, the threshold limit for ozone was recently revised downward from 1 ppm. to 0.1 ppm. by the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists. Concentrations below 0.1 ppm. are discomforting to some individuals because of the disagreeable odor of ozone. Considerable variation in odor threshold, as well as in susceptibility to headache and eye and throat irritation is common among individuals, but most can detect the odor of ozone at a few hundredths of a ppm., a level well below the threshold limit for general comfort.

Effects of Age

The age of the animal has been repeatedly found to have an important effect on the acute toxic response to ozone exposures. Results of representative experiments in mice in Table IV show that 4 ppm. ozone for 4 hrs. was at least an LD_{50} for young, 19 g, white mice, whereas the same exposure in old mice was almost without effect in producing mortality in groups of equal numbers of animals. A similar effect has been reported for the respiratory irritant sulfur dioxide (17); 1-2 mo.-old guinea pigs died after 8-hr. exposure to 19 mg/m^3, but 50 mg/m^3 were required to kill 1-1.5 year-old animals.

Respiratory Infection

It is a common finding to observe that exposures to ozone *bring out* or activate latent, subclinical respiratory infections in animals, resulting in a full-blown respiratory disease that often ends fatally. The concentrations of ozone responsible for this exacerbation were around 1 ppm., concentrations incapable in themselves of producing fatal respiratory injury. This characteristic associated with ozone has been observed in the rodent species on autopsy following ozone exposure.

Intermittent Exposures

In an effort to discover means of reducing the unfavorable responses to ozone, the effect of intermittent exposure to ozone was investigated. Adult male white mice were subjected to inhalation of ozone at 4 ppm. for 30 min, alternated with 20-min exposures to air. The total time of exposure to ozone was 4 hrs, an exposure capable of killing at least 50% of the animals if administered without interruption for 4 hrs. The results of a representative experiment given in Table V show indeed that interrupted exposure to ozone reduces the fatal effects of ozone in mice and

TABLE IV

Effect of Age On Susceptibility To Ozone Toxicity

Male Mice 4-Hr. Exposures

Conc'n. of Ozone[a]	Mortality Numerator: No. of Animals dead, Denominator: No. of Animals exposed	
ppm. by vol.	Young Mice, 19g	Old Mice, 35g
4 Expt. I	6/8	0/8
4 Expt. II	5/10	1/10

(a) Nitrogen oxide concentration averaged 0.1 ppm.

TABLE V

Effect On Animal Toxicity of Interrupted Ozone Exposures

Male Mice, 20g

Ozone Conc'n.	Mortality Numerator: No. Animals Dead Denominator: No. Animals Exposed
ppm. by vol.	30 min. Ozone, 20 min. air.
4	Total 4-hr. Exposure to Ozone 2/10
4	Continuous 4-hr. Exposure to Ozone 6/10

indicates a means of reducing the effects of this hazardous substance.

Prophylaxis of Ozone Toxicity

Pursuing the study of the means of reducing or preventing the toxic effects of ozone, we tested various reducing agents on the hypothesis that they might combat a potent oxidizing agent, ozone. Table VI shows that when vitamin C is administered prior to exposures to lethal concentrations of ozone, but not after, it is effective to a measurable degree in reducing mortality of exposed mice. The vitamin C was administered intraperitoneally in saline in amounts of 10 mg/mouse. Mercaptoethylamine, a reagent of claimed efficacy in radiation injury and in high-pressure oxygen toxicity, increased the mortality from ozone exposure. On the other hand, fortifying the vitamin C with other vitamins and reducing agents such as pantothenate, cysteine, glycuronate, glycine and glutamate resulted in almost complete protection against fatal ozone exposures. It is important to note that the occasional animals that did not survive the treatment died uncharacteristically several days following the ozone exposure, indicating death was due to causes other than ozone injury, presumably infection, that could be prevented by administration of suitable antibiotics; small animals, succumbing to the effects of ozone exposure, regularly die within 24 hrs. after the start of exposure. The prophylactic effect of vitamin C has been independently confirmed by another investigator in our laboratories.

It is of more than passing interest to note that the capacity of the reducing mixture to prevent the effects of nitrogen dioxide was less than that for ozone, indicating a different mode of action on the lung of nitrogen dioxide.

Interesting as the foregoing findings are, they scarcely compare in significance with the following two aspects of ozone toxicity, namely: *1.* Effects of physical stress. *2.* The marked tolerance acquired in animals following shortly after brief exposures to noninjurious levels of ozone.

Enhancement of Toxicity from Physical Activity

When rodents were subjected to the physical activity imposed on them by being in a motor-driven rotating cage, while at the same time being exposed to otherwise noninjurious concentrations of ozone, the animals died of the combined effects, with a typical ozone toxicity response of pulmonary edema and hemorrhage. Atmospheres containing 1 ppm. ozone caused death of animals being exercised in a rotating cage at 7 rpm. for 15 min. each hr. for 6 hrs. total exposure. These results are shown in Table VII. It is seen that no amount of repeated daily 6-hr. exposure to this concentration of ozone up to 200 days without exercise produced any mortality or any observable change in the exposed rats (data line 1). On the other hand, subjecting the animals to exercise while inhaling ozone proved to constitute an LD_{50} within 6 hrs. for the exposed adult rats of different ages (data lines 2 and 3). Exercise alone on rotating cage was without effect as shown in the last data line

TABLE VI

Effect of Reducing Agents On Ozone and Nitrogen Dioxide Mortality In Mice

Agent	Reducing Agent		Saline Control	CT Value ppm.-hrs.
	Before Ozone Exposure	After Ozone Exposure		
	Ozone			
Vitamin C. Expt. I	5/10	8/10	8/10	50
Expt. II	1/10		4/10	30
B-Thiolamine[a]				
Expt. I	10/10		2/10	24
Expt. II	10/10		5/10	26
Reducing Mixt.[b]	3/10[c]		9/10	42
	Nitrogen Dioxide			540
Reducing Mixt.	3/10		7/10	600
Reducing Mixt.	5/10		10/10	

(a) B Mercaptoethylamine, courtesy Squibb Institute, New Brunswick, N. J.

(b) Courtesy J. B. Roerig & Co., Chicago, Ill., consisting of vitamin C, cysteine, potassium glycuronate, calcium pantothenate, glycine and sodium glutamate.

(c) The deaths of these animals were believed not due to ozone but to respiratory infection, as they occurred atypically several days after the usual time and are presumably preventable by antibiotic treatment.

TABLE VII

Increase of Ozone Toxicity from Superimposed Exercise
Ozone Concentration: 1 PPM. By Volume

Exercise: 15 min./hr. 7 rpm.

No. Animals	Av. Body Wt. Gm.	Treatment		Mortality Numerator: No. Animals Dead Denominator: No. Animals Tested
		Ozone	Concurrent Exercise	
25	230-380	200 days, 6 hr. daily	No	None (0/25)
10	144	6 hrs.	Yes	6/10
10	264	6 hrs.	Yes	5/10
10	250	No	Yes	None (0/10)

in Table VII. Mice responded similarly.

Development of Tolerance

Perhaps the most striking and unusual feature of ozone toxicity is the marked tolerance to multilethal doses of ozone that develops in rodents after brief exposures to ozone. Increased tolerance to ozone was first observed in rats that had been previously exposed for many days to 1 ppm. ozone and then challenged in the rotating cage while being exposed to ozone as described above; the anticipated number of deaths did not occur. These results are shown in Table VIII, data lines 1, 2. It is seen that the longer the animals were given previous exposure to 1 ppm. only, the longer the survival on repeated challenging exposures to ozone with exercise.

In an effort to determine the minimal time of ozone exposure required for the rats to develop significant tolerance, successively shorter periods of ozone pre-exposure were tested, from 18 hrs. to 1 hr. It is seen that tolerance to ozone is successively decreased in degree when pre-exposure is thus shortened, although some tolerance is demonstrated with as little as 1-hr. pre-exposure to 1 ppm. ozone (data lines 9 and 10). Tests for tolerance were made 24 hrs. after the start of the initial exposure, thus demonstrating the very rapid development of ozone tolerance. Because the 6-hr. exposure to 1 ppm. ozone developed a reproducible tolerance of significant degree, 6 hrs. was taken as a convenient preexposure time for subsequent studies to determine the duration of tolerance to ozone from a single exposure.

Duration of Tolerance to Ozone

Tolerance to ozone lasting for 4 to 6 wks. was developed in rats from a single 6-hr. exposure to 1 ppm. ozone. For this demonstration a large group of adult male albino rats was given a single, 6-hr. exposure to 1 ppm. ozone. From this group, smaller groups of 10 rats each were subsequently tested for tolerance, as described above, after one day, and 1, 2, 3, 4 and 6 wks.

All the rats given a single, 6-hr. exposure to ozone showed tolerance to otherwise lethal exposures whether challenged on the day following the 6-hr. exposure, or one week, 2, 3, or 4 wks. later. Rats challenged on the 6th week, however, died (7 of 10 exposed), showing that ozone tolerance may extend over a period of from 4 to 6 wks. Controls not previously exposed to ozone when placed in the same activity cage with ozone-exposed animals, died either during ozone exposure in the activity cage (*i.e.*, within 6 hrs.) or shortly thereafter. Rats exposed 6 hrs. to 1 ppm. ozone and then subjected the next day to exercise only in the activity cage with no ozone showed no mortality or any untoward effects ascribable to either the exercise or the previous day's exposure to ozone.

In order to make further assurance that the tolerance observed in the activity cage experiments was real and not the result of some unsuspected or adventitious finding associated with the conditions of the experiment, rats with a previous exposure to ozone were later challenged by exposure to ozone alone at multilethal doses (7-11 ppm. ozone). No previously exposed rat succumbed to a 4-hr. exposure, whereas all rats with no previous exposure to ozone died. On autopsy, the tolerant rats showed no pulmonary edema and hemorrhage, whereas this was the cause of death in the nontolerant rats. It is of interest to note the characteristic spasmodic breathing of animals exposed to lethal concentrations of ozone was still present in the tolerant animals.

In preliminary experiments no *spread* of tolerance to ozone appeared to occur among rats that had previously been exposed to either nitrogen pentoxide or hydrogen peroxide and then challenged in the usual way to ozone combined with exercise. Further work will have to be done, however, to confirm these preliminary observations.

It is of interest to note in relation to the mechanism of tolerance development that no tolerance in rats was acquired from single intraperitoneal exposures to ozone, thus pointing to a reaction characteristic of lung tissue in the development of ozone tolerance.

Effect of Alcohol on Tolerance

A most interesting effect of alcoholic ingestion on the development of tolerance to ozone was demonstrated in the following way. Rats given water containing 10% ethyl alcohol by volume as the sole liquid intake for 6 wks. were exposed to 1 ppm. ozone for 6 hrs. by the usual procedure for the development of tolerance. When subsequently tested for tolerance 2 wks. later by quiescent exposure to 8 ppm. ozone, all 5 of 5 rats tested succumbed showing no tolerance to ozone at this time. A

TABLE VIII

Development of Tolerance to Ozone As Shown By Pre-Exposure To Ozone Followed By Exercise During Ozone Exposure All Ozone Concentrations 1 ppm. by Vol.

Exercise: 15 min./hr. 7 rpm. Exposure: 6 hrs. daily, unless otherwise indicated.

No. Animals	Av. Body Wt.	Pre-exposure to Ozone (Without Exercise)	Mortality On Subsequent Days of Exposure to Ozone with Exercise. Numerator: No. of Animals Dead. Denominator: No. of Animals Tested.					
	gm.	Hrs.	Days: 1	2	3	4	5	6
9	236	90	0/9	0/9	0/9	3/9	0/6	3/6
10	304	150	0/10	0/10	0/10	0/10	0/10	1/10
10	258	18	0/10	0/10	0/10			
3	240	—	2/3	0/1	0/1			
10	248	6	0/10	0/10	1/10			
3	245	—	2/3	0/1	0/1			
10	251	3	0/10	2/10				
2	245	—	1/2	0/1				
10	212	1	1/10	1/9	1/8			
3	210	—	1/3	0/2	0/2			

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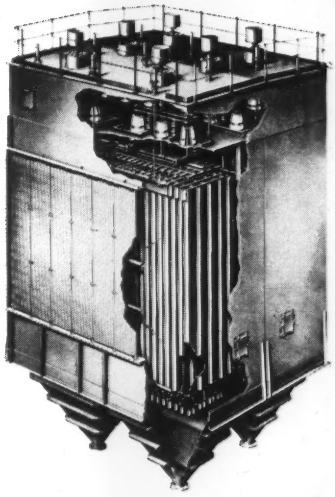

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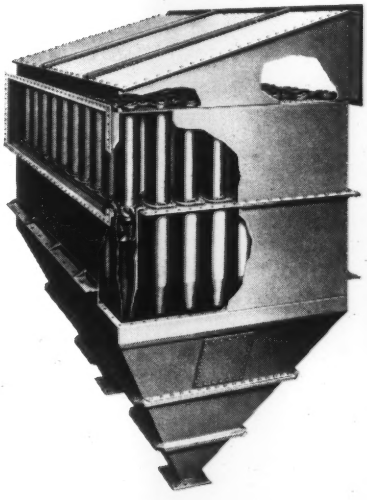

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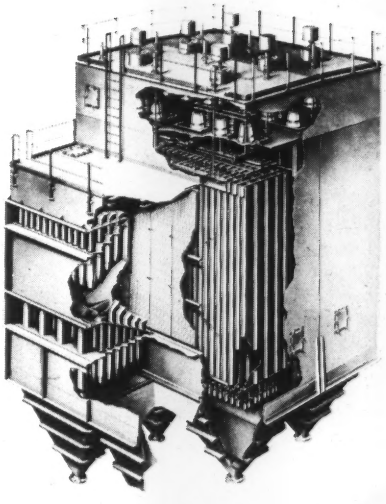

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similar group of 5 controls with no prior exposure to ozone died as expected. This interesting finding is being explored.

Discussion

From evidence introduced here (Table I) and elsewhere [3,4], ozone can no longer be seriously denied to be one of the more highly poisonous gases. The rapidly lethal effects in small animals from exposure to a few ppm. by volume of pure ozone, the aggravation of the ozone effects in exercised animals, and the pulmonary involvement in shielded arc-welders to relatively low concentrations of ozone, all attest to its highly injurious character. Oxides of nitrogen have been shown to be associated contaminants, both in certain types of smogs, and in ozone industrially produced from air by means of electric discharge, and thus must enter into any consideration of the toxicity of ozone that is found in either of these instances. A critical review of the toxicities of nitrogen oxides with regard for the amounts that may accompany the production of ozone, however, reveals no convincing evidence that the oxides of nitrogen contribute significantly to the toxic effects of ozone (Table II). The most interesting and important findings reported here are the many ways in which the highly injurious effects of ozone may be increased, reduced, or even abolished. The increased susceptibility to the lethal effects of ozone of the very young of several species of animals, compared with the ages of the species is readily demonstrable, and is appreciable (Table IV). The increased response to pulmonary irritation found in early age is not unique for ozone, but is well documented for the upper respiratory irritant, sulfur dioxide[14].

The enhancement of ozone injury in animals by activity during exposure to ozone has been the most striking demonstration of all. The lethal outcome of otherwise noninjurious concentrations of ozone results undoubtedly from a multiplicity of factors in addition to that of the more obvious reactions associated with activity such as increased respiration and circulation rates. Hormonal releases, for example, in the form of catechol amines, epinephrine and norepinephrine, as well as in certain adrenocorticosteroids (compounds B and F) have been reported in tumbled rats[18], a condition not completely unrelated to that in our cage-activated rats especially during the terminal phases on the exposure. How much of a role these hormones play in these experiments, however, still remains to be determined.

Methods of reducing or abolishing the fatal effects of ozone were also numerous. Pulmonary changes associated with aging resulted in the capacity of the host to resist otherwise fatal doses of ozone. Whether this is due to increased thickening of the alveolar septa with age, reduced metabolic rate, or to other factors is under study in our laboratories, at the present time. Interrupted exposure to ozone acts to the advantage of the host and, although not particularly striking in the manner demonstrated in our experiments, the interrupted exposure techniques could be utilized to decisive advantage in protecting individuals against injurious ozone exposures. During interruptions presumably tolerance to ozone would be developing.

It is interesting, we think, that the grave effects of pulmonary edema and hemorrhage from acute exposure of ozone may be prevented in animals by so simple a procedure as a combination of vitamins and reducing agents prior to ozone exposure (Table VII). The clues furnished by such substances on the mechanism of action of ozone, and related oxidative pulmonary irritants such as nitrogen dioxide are considerable; from such information a definitive hypothesis of action of these pulmonary irritants may be formulated and tested.

The finding of marked tolerance in animals to ozone, developing rapidly and enduring long, may have considerable bearing on responses of populations to ozone - containing smogs. Several factors indicate this. *1.* No human symptoms referrable to ozone action have been noted in Los Angeles-type smog, despite reports of significant ozone levels. *2.* Ozone tolerance of measurable degree was noted in animals exposed for but 1 hr. to 1 ppm. *3.* Ozone is a rather ideal substance for epitomizing the toxicologic concept, CT = K (*i.e.* equal mortalities resulted in animals exposed to 4 ppm. ozone for 6 hrs. (CT = 24 ppm.-hrs.) or to 50 ppm. for 0.5 hrs. (CT = 25 ppm-hrs.). Thus it would not seem to represent too great an extrapolation of the data to assume that if tolerance develops at 1 ppm. for 1 hr. that some tolerance could conceivably develop at 0.1 ppm. for 10 hrs. Further if the response of the human lung to ozone may be assumed to be similar to that of the animals tested in these studies, one might reasonably conclude that no acute effects on human populations would be expected from ozone exposures occurring in Los Angeles-type smog, owing to the often repeated exposures to very low-grade ozone concentrations, of the order of a few tenths ppm.

Summary and Conclusions

Experimental evidence is presented that ozone in single, acute exposure is a highly poisonous substance to laboratory animals. No experimental evidence was found that this toxicity is modified to a significant degree by the presence of nitrogen oxides that may accompany ozone production.

Seven factors have been experimentally found that may modify the toxicity of ozone. Four of these, youth, physical exertion, alcohol and respiratory infection, tend to augment the injurious response or act to the detriment of the host; the remainder, intermittent exposure, premedication, and preexposure either reduce or eliminate the injurious effects of ozone. Consideration has been given these factors in the evaluation of possible acute hazards to populations from ozone-containing smogs.

Acknowledgment

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References

1. A. J. Haagen-Smit, C. E. Bradley and M. M. Fox. Formation of Ozone in Los Angeles Smog. *Proc. 2nd Natl. Air Poll. Symp.*, Pasadena, Cal., 1952.
2. E. R. Stephens, P. L. Hanst, R. C. Doerr and W. E. Scott. Reactions of NO_2 and Organic Compounds in Air at Concentrations of ppm,, presented at 128th Nat'l. meeting of Am. Chem. Soc., Minneapolis, Minn., Sept. 1955.
3. H. E. Stokinger. Toxicity of Ozone. *A.M.A. Arch. Ind. Hyg.* **9**, 366, (1954).
4. M. Kleinfeld, Clinical Effects Associated with Inert-Gas Shielded Arc Welding. Presented before the Am. Acad. Occup. Med., Cincinnati, Feb. 16, 1956.
5. C. S. Weil. Tables for Convenient Calculation of Median Effective Dose. *Biometrics* **8**, 249, (1952).
6. O. Rebmann, A New Pest Exterminator. *Zschr. Gesundhtechn. Stadthyg.* **25**, 279, (1933).

7. E. O. Jordan and A. J. Carlson. Ozone, its Bactericidal, Physiologic and Deodorizing Action. *J. Amer. Med. Ass.*, **61**, 1007, (1913).

8. R. G. Smith and P. Diamond. The Microdetermination of Ozone. *A.I.H.A. Quart.*, **13**, 235, 1952.

9. D. H. Byers, B. E. Saltzman and F. L. Hyslop. Described in *Design of Referee Method for Determination of Ozone.* By M. Storlazzi. Final Report of Environment Research Laboratory, Dept. of Public Health, School of Medicine, Univ. of Washington, May 10, 1955.

10. B. E. Saltzman. Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere. *Anal. Chem.* **26**, 1949 (1954).

11. B. E. Saltzman, D. H. Byers and F. L. Hyslop. Nitrogen Oxide Impurities in Ozone. *Ind. Eng. Chem.* **48**, 115, (1956).

12. C. E. Thorp. Influence of Nitrogen Oxides on the Toxicity of Ozone. *News Ed. Am. Chem. Soc.* **19**, 686 (1941).

13. C. E. Thorp. The Toxicity of Ozone. *Ind. Med. Surg.* **19**, 49, (1950).

14. W. F. von Oettingen. The Toxicity and Potential Dangers of Nitrous Fumes, Pub. Health Bull. No. 272, *U.S.G.P.O.*, Wash. (1941).

15. LeB. E. Gray, F. M. Patton, S. B. Goldberg and E. Kaplan. Acute Inhalation Toxicity of Nitrogen Dioxide. *Arch. Ind. Hyg.* **10**, 418, (1954).

16. W. M. Diggle and J. C. Gage The Toxicity of Ozone in the Presence of Oxides of Nitrogen. *Brit. J. Ind. Med.* **12**, 60, (1955).

17. I. Greenwald. Effects of Inhalation of Low Concentrations of Sulfur Dioxide upon Man and Animals, *A.M.A. Arch. Ind. Hyg.* **10**, 455 (1954).

18. J. McLaughlin, Jr. and I. Gray. Corticosterone, 17-Hydroxy-Corticosterone Epinephrine & Norepinephrine Levels in Plasma of Rats Subjected to Tumbling Trauma. Presented at 128th meeting of the Am. Chem. Soc., Minneapolis, Minn., Sept. 1955.

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The Chemistry of the Oxides of Nitrogen in the Upper Atmosphere and the Results of A Continent-Wide Precipitation Chemistry Program for the Analyses of NO_3^- and NH_4^+ in Rain Water*

LEWIS E. MILLER
Geophysics Research Directorate
Air Force Cambridge Research Center
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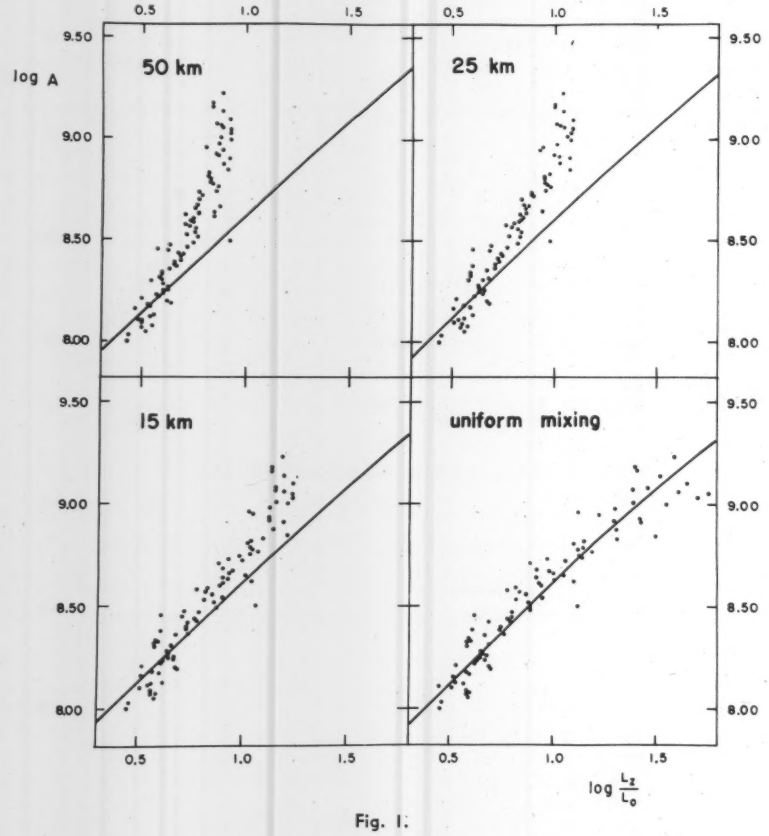


Fig. 1.

Courtesy of Dr. Leo Goldberg and Edith A Müller, McMath-Hulbert Observatory, University of Michigan

Empirical curves of growth for N_2O assuming that N_2O is concentrated in a layer of uniform density 5-km. thick at altitudes of *(a)* 50, *(b)* 25, and *(c)* 15 km., and *(d)* that that N_2O has the same vertical distribution as the main body of the atmosphere.

The relation between the total absorption of a line and its integrated absorption coefficient defines the so-called curve of growth. The ordinate (log A) is the logarithm of the total absorption in sec.$^{-1}$. The abscissa is the log L_s/L_o (path length in air masses).

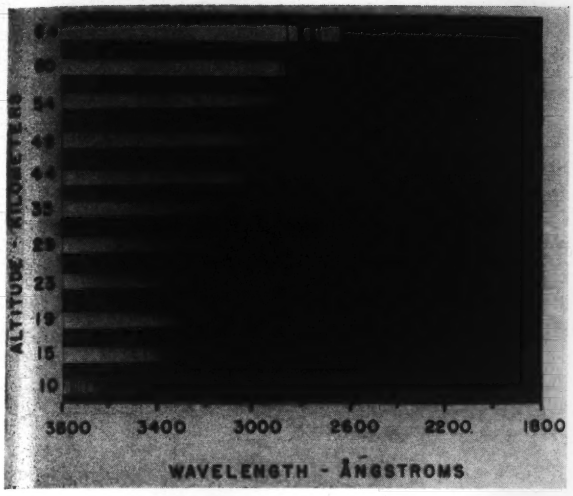
The solid line in the lower, linear end of a theoretical curve of growth for pure collisional broadening with $\gamma/2\ \Pi = 2.0 \times 10^9$ sec.$^{-1}$. It may be observed that for $L_s/L_o > 10$ (Log $L_s/L_o > 1$) uniform mixing is the only graph in accord with the observations, while when the number of air masses is less than four all four assumptions of vertical distribution are in accord with the observations.

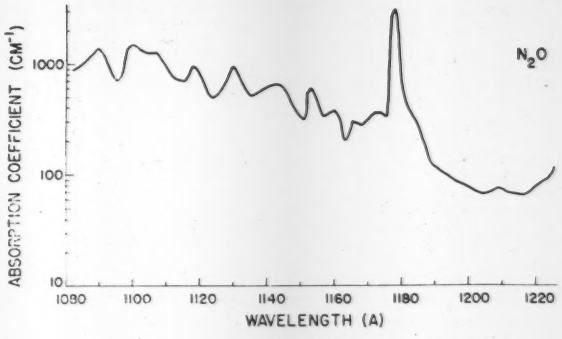
The amount of the oxides of nitrogen that are released daily into the air of the Los Angeles area from the exhaust gases of gasoline-burning vehicles alone has been variously estimated to be from 230 to 800 tons [22]. Nitrous oxide is the only oxide of nitrogen whose presence has been established by direct observational evidence to exist in the upper atmosphere. It is regarded as a permanent atmospheric constituent. It is considered to be completely mixed with and to have the same vertical distribution as the main body of the atmosphere[10]. The basis for this conclusion is illustrated in Fig. 1.

Regardless of the origin of atmospheric nitrous oxide, whether it originates from soil air or from homogeneous gas reactions in the upper atmosphere, the percentage composition by volume of dry air is about 5×10^{-6} % (50 pphm., or 7.6×10^{-6} % by weight. This is equivalent to a path length of 4 mm. at S. T. P. Assuming that the composition is uniform over the entire earth, there are 13.5 tons of nitrous oxide/square mile. Assuming further that the area of Los Angeles is 500 square miles there are then 675 tons of this natural occurring oxide of nitrogen in the air over Los Angeles as compared to 230-800 tons of oxides of nitrogen liberated daily as air pollutants.

It is the purpose of the paper to examine *(a)* the fate of nitrous oxide in the atmosphere, and *(b)* the evidences for the presence of nitrogen dioxide in the air at ground level from the experimental results of a continent-wide investigation of the quantity of nitrate and ammonium ion concentrations in rain water over

*Presented at the 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 8-13, 1957.





(Above) Fig. 3. Absorption coefficients vs wavelength of N_2O in the spectral range λ 1080 to 1220 A.

(Left) Fig. 2. A series of Solar Spectra obtained during a rocket flight by the Naval Research Laboratory 14 June 1949. Note that with increasing altitude and as the concentration of Ozone decreases the spectra extend to shorter wavelengths.

the United States. An answer may be found as to whether the photolysis of nitrous oxide and its dissociation products contribute to air pollution.

The Origin of Atmospheric Nitrous Oxide

Briefly, two theories have been suggested for the occurrence of nitrous oxide in the earth's atmosphere: *(a)* From soil air, and *(b)* From homogeneous gas reactions in the upper atmosphere. Studies of the decomposition of vegetation under aerobic conditions by the action of soil microorganisms by various biologists and biochemists[42,19,38,2] may be considered to have established that soil air is an important source.

Strong evidence also supports the theory that atmospheric nitrous oxide is formed in the upper atmosphere through homogeneous gas reactions. The term, *upper atmosphere* will be used throughout this paper to mean the region from about 50 to 100 km. Probably the two most promising reactions to account for the formation of nitrous oxide in the upper atmosphere result from the following combinations in a region where atomic oxygen and ozone are formed and in equilibrium.

$$O + N_2 + M \rightarrow N_2O + M \qquad (1)$$

$$O_3 + N_2 \rightarrow N_2O + O_2 \qquad (2)$$

These theoretical equations have been discussed by Bates and Witherspoon[6], Goody and Walshaw[11], and Harteck and Dondes[13]. The reactions appear to meet the nitrous oxide requirement. It is probably safe to conclude that the source of atmospheric nitrous oxide is a *both/and* origin in which both soil air mechanisms and homogeneous gas reactions in the upper atmosphere are in operation. Additional data will be needed to decide definitely which source might be considered to be the more important.

The Fate of N_2O In The Atmosphere

The photochemical dissociation of nitrous oxide by ultraviolet light has been studied by many investigators. Nitrous oxide is comparatively transparent and photochemically stable to wavelengths greater than about 2000 A. Knowledge of absorption coefficients, absorption and ionization cross sections of the nitrogen oxides, and the study of absorption spectra in the infrared, ultraviolet and vacuum ultraviolet spectral regions are extremely valuable in deciding the fate of the various nitrogen oxide pollutants of the air.

Leifson[20] using an absorption cell of 15 mm. thickness observed two continuous bands in the absorption spectra of nitrous oxide. The first extended from λ 2000 to 1680 A, while the second was from λ 1500 A to the limit of transparency of the fluorite windows. Macdonald[21], Wulf and Melvin[44], Sen Gupta[37], Duncan[8], and the extensive photochemical studies by Noyes and his collaborators[32,14,33] represent some of the early and fundamental work upon the photochemical dissociation of nitrous oxide in the far, or vacuum ultraviolet. Each of these papers and others of recent date have been summarized and evaluated in an extensize review by Miller[24].

Sponer and Bonner[39] have studied the continuous absorption of nitrous oxide in the long wavelength region of the near ultraviolet. It should be noted that their observations of continuous absorption at wavelengths as great as 3065 A, radiation which would be expected to reach the surface of the earth, required a pathlength of 33 m. of nitrous oxide at a pressure of 1½ to 5 atmospheres as compared to 4 mm. of nitrous oxide normally present in the atmosphere at S. T. P. Fig. 2 shows a series of solar spectra obtained during a rocket flight by the Naval Research Laboratory 14 June 1949. Note that with increasing altitude and as the concentration of ozone decreases in the region between 15 and 60 km. that the absorption increases with a sharp cut-off at about 2900 A.

It appears reasonable to conclude that for wavelengths longer than 2000 A owing to the very weak absorption and the high transparency of nitrous oxide that its dissociation beginning as about λ 3070 A

$$N_2O + h\nu \xrightarrow{\lambda \leqq 3070\ A} N_2 + O\ (^3P \text{ or } ^1D) \qquad (3)$$

and at λ 2400 A

$$N_2O + h\nu \xrightarrow{\lambda \leqq 2400\ A} NO + N\ (^4S) \qquad (4)$$

would be unlikely to occur in the tropospheric levels.

Recent Studies of the Photochemistry Of Nitrous Oxide

Zelikoff, Watanabe, and Inn[45] at the Geophysics Research Directorate

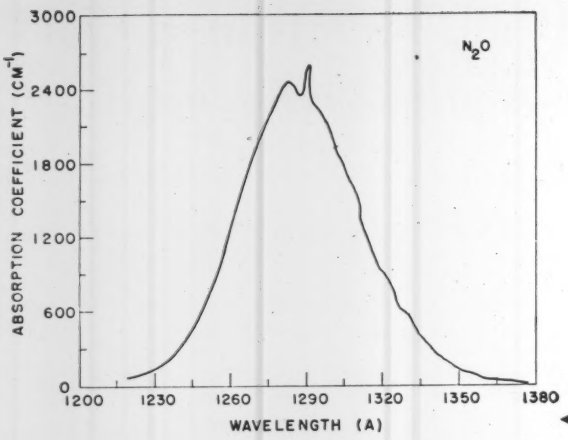


Fig. 4. Absorption coefficients vs wavelength for N_2O in the spectral range λ 1220 to 1380 A.

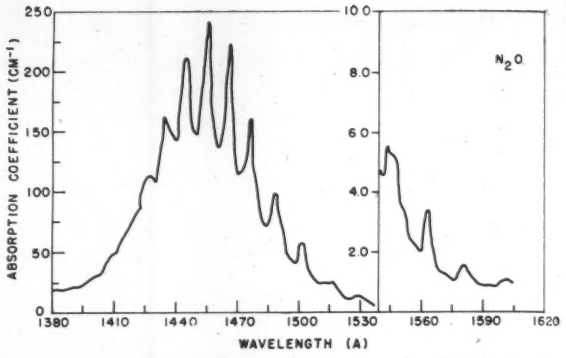


Fig. 5. Absorption coefficients vs wavelength of N_2O in the spectral range λ 1380 to 1605 A.

of the Air Force Cambridge Research Center have made extensive investigations on the absorption coefficients of gases in the vacuum ultraviolet. Four continua were observed for nitrous oxide within the spectral region 2100 A to 1080 A, at 1820 A, 1450 A, 1285 A, and 1080 A. These are shown in Figs. 3, 4, 5, and 6.

In the region from 1080 to 1220 A there are a number of rather diffuse bands upon which is superimposed what appears to be a continuum. At a wavelength of about 1180 A is the strongest ultraviolet absorption band observed for nitrous oxide. The region in Fig. 4 shows a rather smooth continuum with several weak diffuse bands on its long wavelength slope. Fig. 5 shows the continuum between λ 1380 to 1605 A to be composed of numerous bands with a maximum absorption of about 1450 A. The region from λ 1605 to 2100 A is one of weak continuous absorption with a maximum at 1820 A.

The Interpretation Of The Absorption In The Vacuum Ultraviolet

The possible dissociation processes of some of these four continua were interpreted on the basis of a potential energy diagram for nitrous oxide shown in Fig. 7. The accessible electronic levels of nitrous oxide are repulsive. The following are possible primary processes.

$$N_2O\ (^1\Sigma) + h\nu \rightarrow N_2\ (^1\Sigma) + O\ (^3P, {}^1D, \text{or } {}^1S) \qquad (5)$$

$$N_2O\ (^1\Sigma) + h\nu \rightarrow NO\ (^2\Pi) + N\ (^4S) \qquad (6)$$

Later Zelikoff and Aschenbrand[46] of the Geophysics Research Directorate have studied in greater detail the photolysis of nitrous oxide at the wavelengths of 1470 A and 1849 A. The following mechanism was considered most favorable for the dissociation.

$$N_2O + h\nu \rightarrow N_2 + O \qquad (7)$$

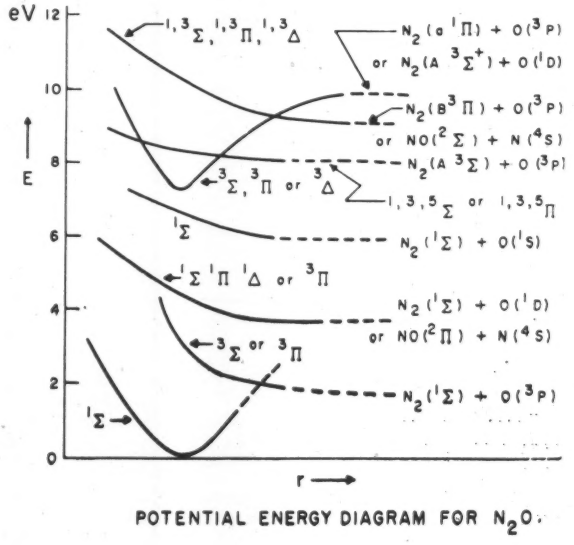
$$N_2O + O \rightarrow 2NO \qquad (8)$$

$$N_2O + O \rightarrow N_2 + O_2 \qquad (9)$$

$$O + O + M \rightarrow O_2 + M \qquad (10)$$

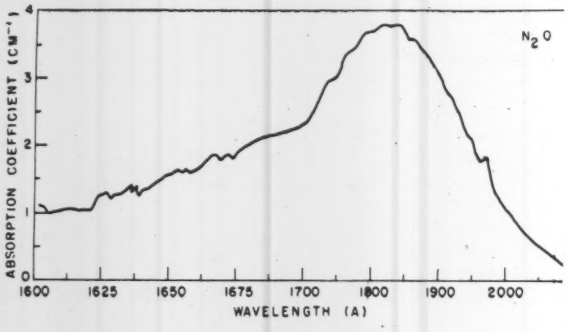
This dissociation mechanism occurs within a wavelength region expected only in the upper atmosphere above the ozone region. Castellion and Noyes[7] have determined the quantum yield of the primary process of equation *(7)* to be one.

Fig. 7. Potential energy diagram for N_2O.



POTENTIAL ENERGY DIAGRAM FOR N_2O.

Fig. 6. Absorption coefficients vs wavelength for N_2O in the spectral range λ 1605 to 2100 A.



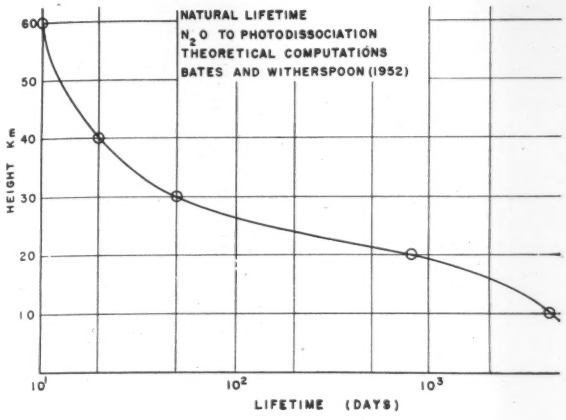
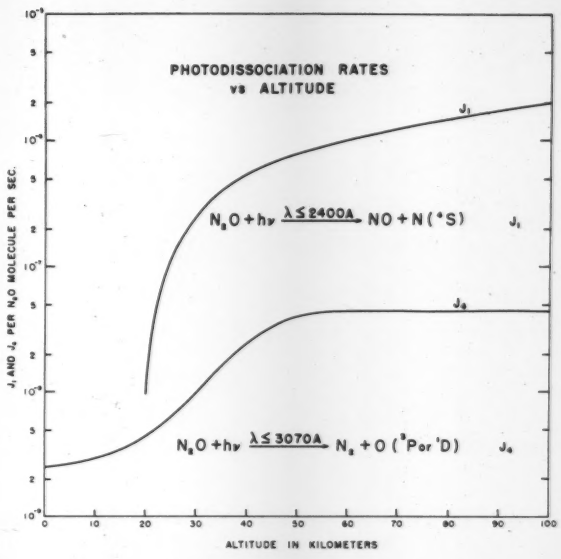


Fig. 7-A.

Fig. 7-B.


PHOTODISSOCIATION RATES
vs ALTITUDE
J_1 AND J_4 PER N_2O MOLECULE PER SEC.
$N_2O + h\nu \xrightarrow{\lambda \leq 2400A} NO + N(^4S)$ J_1
J_4
$N_2O + h\nu \xrightarrow{\lambda \leq 3070A} N_2 + O(^3P \text{ or } ^1D)$ J_4
ALTITUDE IN KILOMETERS

Nitric Oxide In The Upper Atmosphere

Nitric oxide is considered to be an important atmospheric constituent above about 50 km. The photoionization of nitric oxide occurs abruptly at λ 1345 A, or 9.20 $\pm$ 0.02 e. v. The D-region of the ionosphere is attributed to this ionization. However, there is no direct experimental evidence for its presence in the upper atmosphere. Consequently any discussion about either the formation or dissociation of nitric oxide in the upper atmosphere can only be speculative.

Migeotte and Neven[23] were unable to find atmospheric nitric oxide from infrared studies of the solar spectra at the Jungfraujoch Observatory, Switzerland. They concluded that no more than 0.02 cm. at S. T. P. could be present in the earth's atmosphere which determines an upper limit for the abundance of this oxide of nitrogen at about 5×10^{17} molecules/cm^2 column.

The Formation And Loss Of Nitric Oxide

The formation of nitric oxide in the high regions of the atmosphere may result from the primary process

$$N + O + M \rightarrow NO + M \quad (11)$$

Nitric oxide may also be formed from the dissociation of nitrous oxide and the subsequent reaction of atomic oxygen with nitrous oxide as shown in equations *(7)* and *(8)*. The occurrence of reaction *(6)* is controversial. Mitra[25] has found equation *(6)* to be less relatively important in the production of nitric oxide in the 50-100 km. region of the atmosphere.

The numerous reactions for the formation and loss of nitric oxide have been discussed by Bates[4] and Bamford[3]. Bates found a rate coefficient of the order of 10^{-7} sec^{-1} for the reaction

$$NO\ (X\ ^2\Pi) + h\nu \xrightarrow{\lambda\ 2050\text{-}2450\ A} NO\ (A\ ^2\Sigma^+ \text{ or } C\ ^2\Sigma^+) \quad (12)$$

$$NO\ (A\ ^2\Sigma^+ \text{ or } C\ ^2\Sigma^+) \rightarrow N + O$$

In the presence of atomic oxygen the following reaction is believed to be involved.

$$NO + O \xrightarrow{k_1} NO_2 + h\nu \quad (13)$$

The absorption cross-section for the reverse of this reaction has been measured by Holmes and Daniels[15]. Bates has estimated the reaction rate constant, k_1, at most to be about 10^{-17} cm.^{3} sec.$^{-1}$. A larger value of 10^{-15} cm.^{3} sec.$^{-1}$ was assumed by Gaydon[9] for this constant.

Nitric oxide when present in the ozone region (ozonsphere) may be oxidized according to

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2 \quad (14)$$

for which the reaction rate according to Johnston and Crosby[17] is about 8×10^{-15} cm.^{3} sec.$^{-1}$ at 250° K, and the activation energy is 2.5 kcal. Nicolet[29,30] and Mitra[25] have considered the problem of nitric oxide in the upper atmosphere. The time of dissociation of nitric oxide during the day was found to be of the order of 10^7 seconds when derived from rate coefficients of the following equations.

$$NO + h\nu \xrightarrow{k_3} N + O \text{ (rate coeff. } 10^{-7} \text{ sec.}^{-1}) \quad (15)$$

$$NO + N \xrightarrow{k_4} N_2 + O \text{ (rate coeff. } 10^{-17} \text{ cm.}^3 \text{ sec.}^{-1}) \quad (16)$$

This is in a region in which the ratio $n(N)/n(NO) << 1$. Atmospheric mixing tends to prevent nitric oxide from reaching full equilibrium during its long life-time.

Nitrogen Dioxide

From the rate coefficients of dissociation on nitrogen dioxide from the equations,

$$NO_2 + h\nu \xrightarrow{k_5} NO + O \text{ (rate coeff. } 5 \times 10^{-3} \text{ sec.}^{-1}) \quad (17)$$

and

$$NO_2 + O \xrightarrow{k_6} NO + O_2 \text{ (rate coeff. } 10^{-17} \text{ cm.}^3 \text{ sec.}^{-1}) \quad (18)$$

the rate of photodissociation is so rapid during the day that there is little effect upon the nitric oxide concentration. The time of dissociation of nitrogen dioxide is about 200 seconds.

The presence of nitric oxide in the upper atmosphere with reference to

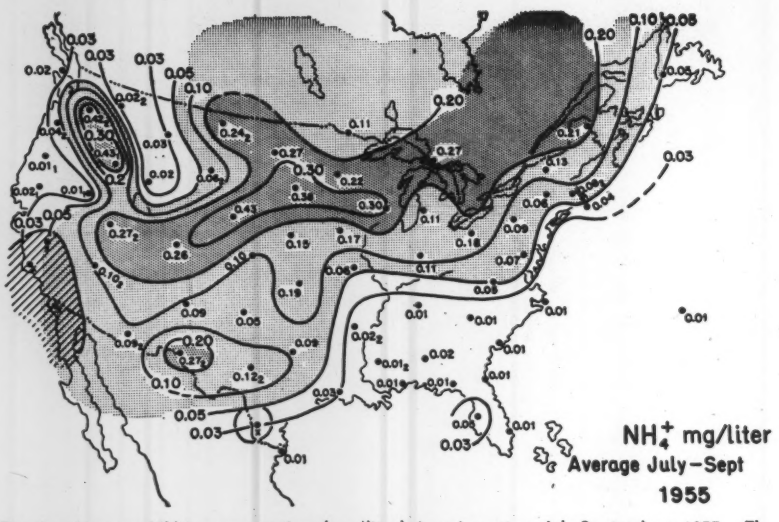


Fig. 8. Average NH_4^+ concentration (mg/liter) in rain water, July-September, 1955. The subscripts indicate the number of months upon which the average was based. No subscript indicates three months. The hatched area indicates no rainfall or insufficient sample.

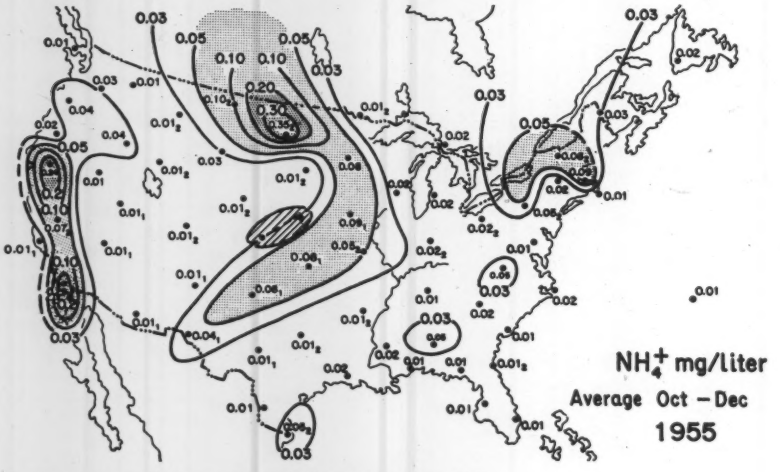


Fig. 9. Same as Fig. 8, except for October-December 1955.

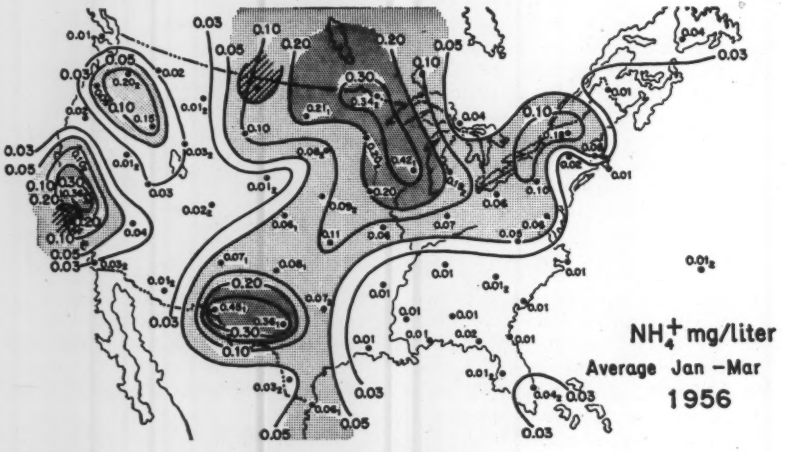


Fig. 10. Same as Fig. 8, except for January-March 1956.

ionization mechanisms[43] has fostered much fruitful research upon the absorption and photoionization cross sections of this oxide in the Lyman-alpha region (λ 1215.7 A).

$$NO + h\nu\ \lambda\ 1100\text{-}1300\ A \longrightarrow NO^+ + e^- \qquad (19)$$

The role of the nitrogen oxides in the airglow has instigated additional theoretical study, and possible explanations for the reactions involving the oxides of nitrogen. The reactions believed to be important according to Nicolet[31], and Pressman and others[34] are: (a) the bi-molecular association of equation *(20)*,

$$NO + O \rightarrow NO_2 + h\nu \quad (3700\text{-}4000\ A) \qquad (20)$$

the luminescence of which was observed by Raleigh[35], later studied by Stoddart[41], by Newman[28] in more detail, and more recently by Neuberger and Duncan[27].

$$(b)\left\{\begin{array}{c} NO_2 + O \rightarrow NO + O_2^* \\ O_2^* \rightarrow O_2 + h\nu \end{array}\right\} \qquad (21)$$

This mechanism *(a)* and *(b)* suggests that nitric oxide functions as a catalyst to provide a continuous source of nitrogen dioxide corresponding to the continuous night airglow. The reaction is somewhat analogous to the photochemical dissociation of nitrogen dioxide

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$
$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (22)$$

in the presence of sunlight yielding a continuous source of atomic oxygen in the lower atmosphere as suggested by Blacet[6], and later by Stephens and others[40]. The regeneration of nitrogen dioxide causes the reaction to be continuous.

The Distribution of Nitrate and Ammonium-Nitrogen in Rain Water over the U. S.

Experimental

During a period of one year from July 1955 to July 1956 rain water was collected simultaneously by a network of some 60 stations over the continental United States, Bermuda, Newfoundland, the Azores, and weatherships over the Atlantic. This was through the cooperation of the U. S. Weather Bureau. The project

was under the supervision of Dr. Junge of the Geophysics Research Directorate of the Air Force Cambridge Research Center who was the contract monitor. The samples were collected under uniform conditions, employing specially constructed rain gauges equipped with a plexiglass funnel which drained into a polyethylene bottle. The sampling was designed to be identical with that of the Scandinavian and European network.

A composite monthly sample was obtained at each station. The details of the sampling and preservation procedures have been described by Junge and Gustafson[18] in the analyses of other constituents, chlorides, *etc.* in rain water. The results of the analyses of 2 components, ammonium and nitrate ion concentrations will be reported here. The principle of the method of the NH_4^+ — N determination involved the distillation of the ammonia in the rain water sample into 0.01 N H_2SO_4. Suitable aliquot portions were Nesslerized with Nessler's Reagent (Folin modification) and subsequently photometric measurement of the color developed at an effective wavelength of 415 mμ. The photometric procedure conformed to the recommended Practice of Photometric Methods for Chemical Analysis of the American Society for Testing Materials (A. S. T. M. Designation X50). The calibration curves were obtained with a Leitz-Rouy Photometer.

The nitrate procedure followed the method for the colorimetric analysis of nitrate ion absorbed from the atmosphere in 0.01 N KOH. The procedure was designed to be used with a photoelectric filter photometer employing a 1 cm. square absorption cell, having polished, plane parallel faces. The photometric practice conformed to the A. S. T. M. Designation X60. A chloroform solution of brucine alkaloid and sulfuric acid were added to the sample. The intensity of the color which was developed was measured at 415 mμ. The readings were actually the sum of both nitrate and nitrite ion concentration. This was used for the NO_3^- — N concentration since only negligible amounts of nitrite were expected to be present.

Upon the examination of monthly maps of the NH_4^+ — N and NO_3^- — N concentration, it was observed that considerable variations occurred which could not be correlated to specific characteristics of the weather.

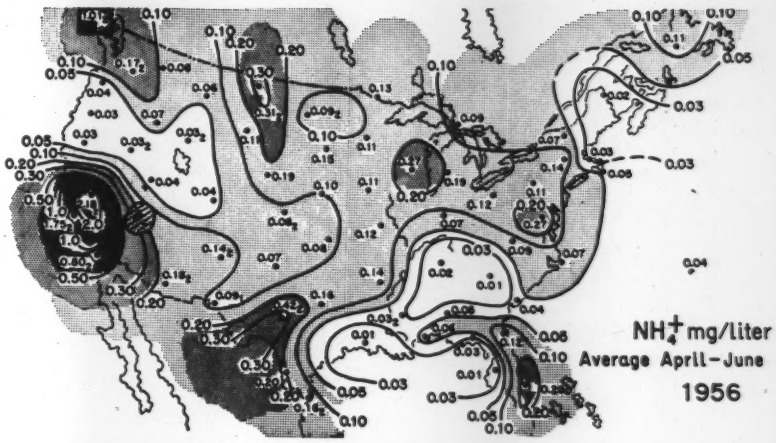
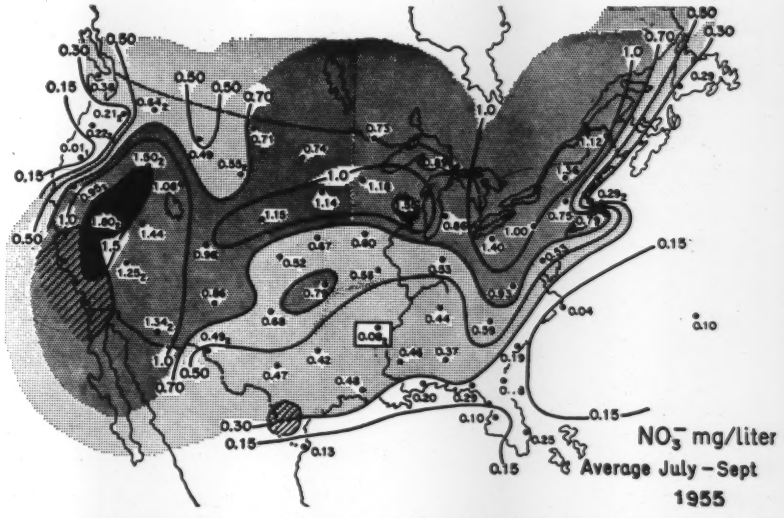


Fig. 11. Same as Fig. 8, except for April-June 1956.



Figs. 12, 13, 14, and 15. Same as Fig. 8, except insert NO_3^- for NH_4^+ and insert the monthly range in the order of Figs. 8, 9, 10, and 11.

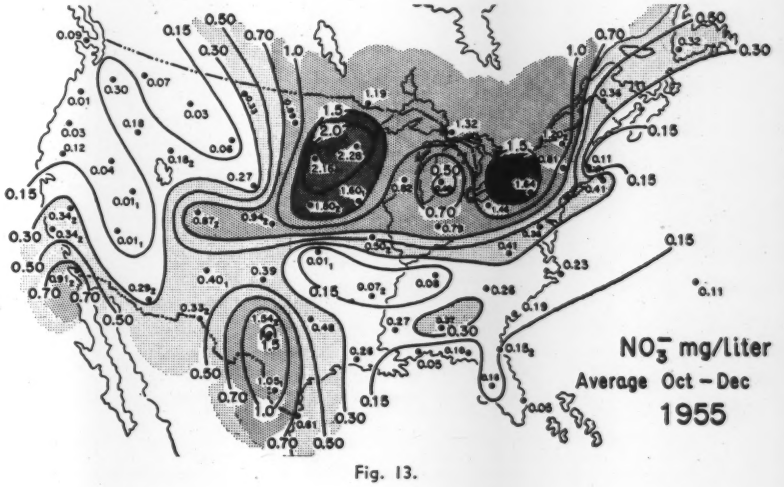


Fig. 13.

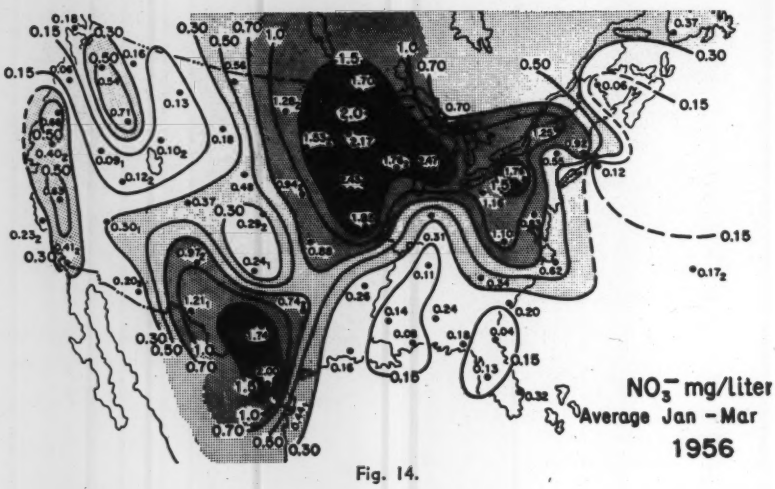


Fig. 14.

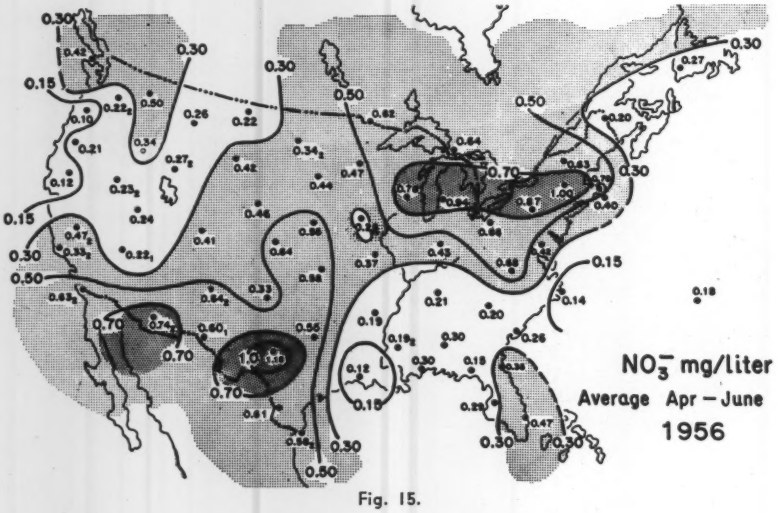


Fig. 15.

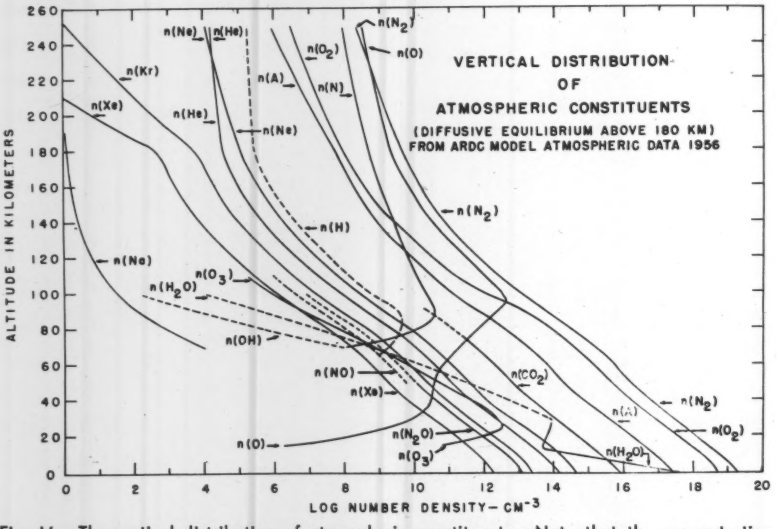


Fig. 16. The vertical distribution of atmospheric constituents. Note that the concentration of N_2O is from one to two orders of magnitude less than the ozone concentration.

Certain features had a tendency to repeat themselves. Consequently quarterly maps, representing the average concentration weighed with respect to the amount of rainfall, were prepared. These are shown in Figs. 8-15.

The Interpretation Of The Maps

The conclusions which may be drawn from these maps with reference to the presence of the nitrogen oxides, such as nitrogen dioxide and possibly nitric oxide, are somewhat limited due to the complexity of rain water chemistry. It should be emphasized that both the NO_3^- — N and NH_4^+ — N may originate from aerosols as well as from gas traces. Normally the aerosols will contain a much higher concentration of nitrogen dioxide and ammonia, present as NO_3^- — N and NH_4^+ — N, than the gas traces, the ratio being about 10:1. It appears likely that a higher fraction from the aerosol material enters the rain is from the gas phase. Therefore it is reasonable to assume that the gaseous and particulate matter constitute about equal parts to rain water. The relationship between the two phases is unknown, and they are likely to have different histories.

An inspection of the maps reveals some interesting correlations with certain geographic parameters. In the first place the major sources of NH_4^+ — N and NO_3^- — N appear to be over land. The high values of NH_4^+ — N appearing along the coast of California and Washington seem to be exceptions on the April-June map. Data from Bermuda, the Azores, and some of the weatherships over the Atlantic (not shown on the maps) are constantly low as compared to the land stations. Generally the concentrations drop against the coastline. A general South-North gradient observed by Angstrom and Högfeld[1] is not confirmed by the maps of our Directorate.

The fixation of nitrogen in rain by lightning (thunderstorms) has often been a controversial issue. The experimental results of Reynolds[36] show no evidence that nitrogen dioxide is formed by the action of lightning, since at no time did the proportion of nitrogen dioxide in the atmosphere increase during thundery weather. Hutchinson[16] and Mukerjee[26] have also reported no correlation between the amount of nitrate concentration in rain water and thunderstorms. The NO_3^- — N maps

of our Directorate indicate no correlation with geographical and distribution of thunderstorm activity. This confirms the conclusion that lightning can only play a negligible role in the nitrogen cycle in the atmosphere.

The pronounced horizontal distribution pattern shown in both the NH_4^+ — N and NO_3^- — N maps suggests that these components come from the lower layers of the troposphere. If a constituent is uniformly mixed throughout the troposphere, we would expect a fairly uniform concentration in rain water. The concentration of the component would also be quite independent of the total monthly amount of rainfall and the geographical location. These conclusions are shown by Junge and Gustafson's report[18] on the chloride distribution within the United States continent, where sea spray particles within maritime air masses soon become uniformly mixed over land by convection. This would exclude the possibility that NO_3^- — N in rain water is produced through photochemical processes occuring in the stratosphere or upper atmosphere. Data on the strontium-90 content in rain water showed a rather similar uniform distribution. The latter data were obtained after a sufficient time lapse of the A-test for uniform mixing to occur throughout the North Hemispheric west wind belt.

A review of the NO_3^- — N maps shows that maxima tend to appear over three geographical areas, *viz.*, *(a)* California and adjacent areas, *(b)* the northern part of the United States, often split by the Great Lakes area, and *(c)* the Western Texas area, except July to September. Minima occur over the northern Rocky Mountain area, and the Northeast.

The maximum over California may be the result of smog in the Los Angeles Basin, which primarily occurs during this season and is known for high nitrogen dioxide concentrations. Industrial activities may account for the high NO_3^- — N concentration east of the Great Lakes, while soil activity, either natural or agricultural may explain the maximum west of the Great Lakes. The fact that the maximum NO_3^- — N concentration over the northern part of the United States is so strong during winter may be due to the stable air stratification. This would enable a higher accumulation of nitrogen dioxide in tropospheric layers, and could provide the necessary time for the formation of the nitrate. The monthly patterns of NO_3^- — N appear to indicate that a time factor is involved for this component varies more than with the other constituents of rain water, and hence fixed to a lesser degree to geographical areas.

There is also the possibility that nitrogen dioxide may be formed by the oxidation of ammonia which would explain some of the similarities to the NH_4^+ — N maps, blurred by a delay in the time factor. Since one source of nitrous oxide in the atmosphere is from soil air, small amounts of the oxides of nitrogen (NO^2 and NO) may be produced directly in the soil through decomposition of existing nitrogen compounds.

Conclusions

Dr. Junge of our Directorate is still engaged in the interpretation of the NO_3^- — N and NH_4^+ — N content of rain water, as well as several other components. The conclusions presented here should be regarded as preliminary and tentative. A more detailed discussion will be published later.

The brief discussion of the recent photochemistry and vertical distribution of the oxides of nitrogen seems to indicate that nitric oxide and nitrogen dioxide formed by the photodissociation of nitrous oxide in the upper atmosphere cannot be expected to diffuse downwards through the ozonosphere to yield any appreciable concentration on the surface of the earth. It may be noted from Fig. 16 that in the ozonosphere the concentration of ozone is one to two orders of magnitude greater than nitrous oxide and its photodissociation products. This would exclude the possibility of these oxides reaching ground level.

The results of the rain yater analyses for NO_3^- — N content also eliminate the possibility of the formation of this component from nitrogen dioxide as a source in high tropospheric levels. The fixation of NO_3^- — N from lightning (thunderstorms) has been shown to have no correlation with the amount of nitrogen dioxide on the earth's surface. As early as 1930 nitrogen dioxide was shown to be a constituent of city air when comparisons were made on urban and suburban, or country, air. Nitrogen dioxide as an air pollutant seems definitely to originate from industrial and man-made activities. However the analyses of the precipi-

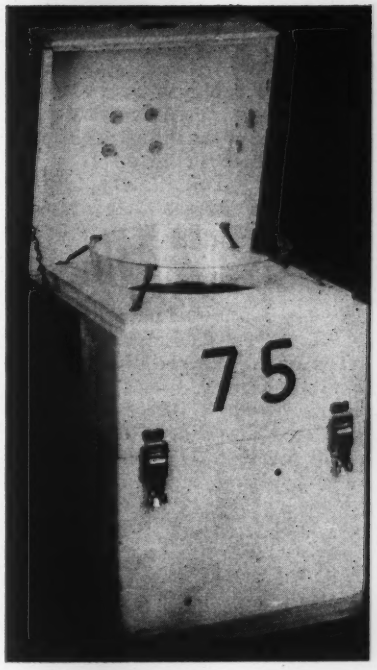


Fig. 17. The specially designed rain gauge used for collecting the rain water samples, showing the plexiglass funnel.

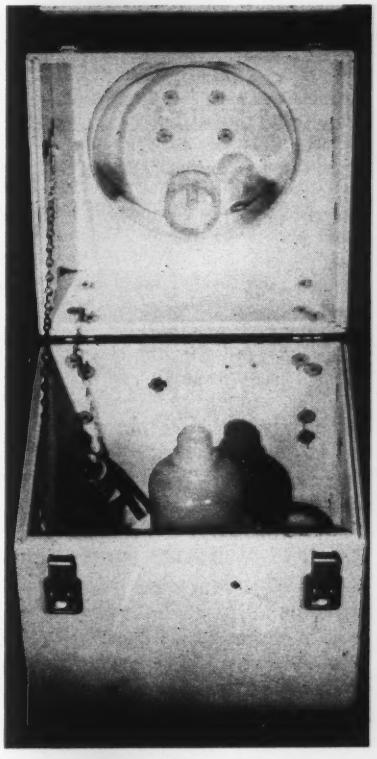


Fig. 18. The interior of a rain gauge showing the polyethylene sample bottle. The electrical heating components melted any snow precipitation.

tation do not give full information concerning the origin, and possible participation of the nitrogen oxides in chemical reactions in the atmosphere. There is need for more quantitative data about the nitrogen compounds present in all levels of the atmosphere. This should help to elucidate the nitrogen cycle in nature, and any contribution to air pollution problems.

Acknowledgment

The author's appreciation is extended to Dr. Chr. E. Junge of the Geophysics Research Directorate of the Air Force Cambridge Research Center for permission to present the rain water data, and for his many helpful discussions.

1. A. Angstrom and L. Högberg. *Tellus* **4**, 33 (1952).
2. P. W. Arnold. *J. Soil Sci.* **5**, 116 (1954).
3. C. H. Bamford. *Reports Progress Phys.* (London) **9**, 75 (1942-43).
4. D. R. Bates. *Ann. geophys.* **8**, 194 (1952); The Earth as a Planet. Edited by G. P. Kuiper, The University of Chicago Press. pp. 583-589, (1954).
5. D. R. Bates and A. E. Witherspoon. *Not. Roy. Astron. Soc.* **112**, 101 (1952).
6. F. E. Blacet. *Ind. Eng. Chem.* **44**, 1339 (1952).
7. G. A. Castellion and W. A. Noyes, Jr. *J. Amer. Chem. Soc.* **79**, 290 (1957).
8. A. B. F. Duncan. *J. Chem. Phys.* **4**, 638 (1936).
9. A. G. Gaydon. *Trans. Faraday Soc.* **42**, 292 (1946).
10. L. Goldberg and E. A. Muller. *J. Opt. Soc. Amer.* **43**, 1033 (1953).
11. R. M. Goody and C. D. Walshaw. *Quart. J. roy. Meteorol. Soc.* **79**, 496 (1953).
12. A. J. Haagen-Smit. *Ind. Eng. Chem.* **48**, No. 12, 65A (1956).
13. P. Harteck and S. Dondes. *Phys. Rev.* **95**, 320 (1954).
14. F. C. Hendriques, A. B. F. Duncan and W. A. Noyes, Jr. *J. Chem. Phys.* **6**, 518 (1938).
15. H. Holmes and F. Daniels. *J. Amer. Chem. Soc.* **56**, 630 (1934).
16. G. E. Hutchinson. *The Earth as a Planet.* Edited by G. P. Kuiper, The University of Chicago Press, 371-433, (1954).
17. H. S. Johnston and H. J. Crosby. *J. Chem. Phys.* **22**, 689 (1954).
18. Chr. E. Junge and P. E. Gustafson. *Tellus* **9**, June No., (1957).
19. M. W. Kriegel. *Geophys.* **9**, 447 (1944).
20. S. W. Leifson. *Astrophys. J.* **63**, 73 (1926).
21. J. Y. Macdonald. *J. Chem. Soc.* 1-14 (1928).
22. P. L. Magill and F. R. Holden. *Air Pollution Handbook.* Mc-Graw-Hill Book Company, Inc., New York. 2-47, (1956).
23. M. V. Migeotte and L. Neven. *Mem. Soc. roy. Sci.*, Liege, 4th series, **12**, 165 (1952).
24. L. E. Miller. The Chemistry and Vertical Distribution of the Oxides of Nitrogen in the Atmosphere. Geophysics Research Paper, No. 39, A. F. C. R. C.-TR, 56-207 (1956).
25. A. P. Mitra. *J. Atm. Terrest. Phys.* **5**, 28 (1954).
26. A. K. Mukherjee. *Indian J. Meteorol. Geophys.* **6**, 57 (1955).
27. D. Neuberger and A. B. F. Duncan. *J. Chem. Phys.* **22**, 1693 (1954).
28. F. H. Newman. *Phil. Mag.* **20**, 777 (1935).
29. M. Nicolet. The Earth as a Planet. Edited by G. P. Kuiper, The University of Chicago Press, 691-699, (1954).
30. M. Nicolet. *J. Atm. Terrest. Phys.* **7**, 152 (1955).
31. M. Nicolet. *J. Atm. Terrest. Phys.* **7**, 297 (1955).
32. W. A. Noyes, Jr. *J. Chem. Phys.* **5**, 807 (1937).
33. W. A. Noyes, Jr. and P. A. Leighton. The Photochemistry of Gases. Reinhold Publishing Corp. p. 328; pp. 397-400 (1941).
34. J. Pressman, L. M. Aschenbrand, F. F. Marmo, A. Jursa and M. Zelikoff. *J. Chem. Phys.* **25**, 187 (1956).
35. Lord Rayleigh (R. J. Strutt). *Proc. Phys. Soc.* **23**, 66 (1910).
36. W. C. Raynolds. *J. Soc. Chem. Ind.* (Trans.) **49**, 168 (1930).
37. P. K. Sen Gupta. *Nature.* **136**, 513 (1935).
38. R. L. Slobod and M. E. Krogh. *J. Amer. Chem. Soc.* **72**, 1175 (1950).
39. H. Sponer and L. G. Bonner. *J. Chem. Phys.* **8**, 33 (1940).
40. E. R. Stephens, P. L. Hanst, R. C. Doerr and W. E. Scott. *Ind. Eng. Chem.* **48**, 1948 (1956).
41. E. M. Stoddart. *Proc. roy. Soc.* **A 147**, 454 (1934).
42. S. A. Wakesman and M. R. Madhok. *Soil Sci.* **44**, 361 (1937).
43. K. Watnabe, F. Marmo and E. C. Y. Inn. *Phys. Rev.* **90**, 155 (1953); ibid. **91**, 436 (1953); **91**, 1155 (1953).
44. O. R. Wulf and E. H. Melvin. *Phys. Rev.* **39**, 180 (1932).
45. M. Zelikoff, K. Watanabe and E. C. Y. Inn. *J. Chem. Phys.* **21**, 1643 (1953).
46. M. Zelikoff and L. M. Aschenbrand. *J. Chem. Phys.* **22**, 1680, 1685 (1954).

Procedures for Making An Inventory of Air Pollution Emissions*

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Public Health Service

Robert A. Taft Sanitary Engineering Center

Cincinnati, Ohio

For an air pollution problem to exist there must be present a source of airborne pollutants and an adversely affected population or environment. Consequently, detailed knowledge of the types and quantities of emissions to the atmosphere is fundamental to an understanding of the nature and magnitude of urban air pollution. The particular degree of definition required in an inventory of emissions is related to the general objectives and scope of the air pollution study.

An emission inventory of an urban community provides such essential information as: *(a)* Relative contribution of the respective sources of pollution to the overall loading of the atmosphere; and *(b)* The relative amounts of each of the different types of pollutants involved. This kind of information is necessary to the intelligent interpretation of results from atmospheric sampling, and for the establishment of a base line against which to relate future trends in air pollution emissions and atmospheric concentrations. Emission data may be utilized to estimate potential atmospheric concentrations of selected pollutants under specified meteorological conditions.

In conducting an emission inventory, sources may conveniently be divided into 2 major classes, specific sources, largely industrial, which are studied on an individual basis and multiple sources, those too numerous to be treated individually. This latter class includes automobiles, trucks, residences, apartments, incinerators and many other sources which collectively contribute significantly to urban air pollution.

* Presented at the 50th Annual Meeting of the Air Pollution Control Association, held at St. Louis, Mo., June 2-6, 1957.

For purposes of illustration, the following discussion will be limited to a description of the air pollution emission inventory presently under development as part of the Special Air Pollution Study of Louisville-Jefferson County, Kentucky. This is a 2-year study, initiated in January 1956, under the technical direction of the Community Air Pollution Program of the Public Health Service, Taft Sanitary Engineering Center, Cincinnati, Ohio, in cooperation with other Federal agencies as well as County and City agencies with substantial financial assistance from local industries.

Multiple Source Inventory

The purpose of the Multiple Source Inventory is to determine the collective contribution to atmospheric pollution from all major emitters which, for practical reasons, are not assayed directly on an individual basis.

Transportation

In a typical American community one of the most important multiple sources of air pollution is the motor vehicle. This opinion is based on considerations not only of total quantity of emissions involved but also of the nature of the pollutants which, according to the latest theories, are capable of entering into photochemical reactions which produce objectionable effects.

Auto exhaust contains significant quantities of nitrogen oxides, sulphur oxides, aldehydes, ammonia and aerosols. Additives to gasoline and oil give rise to other pollutants such as compounds of lead. In addition, large quantities of gasoline vapors are emitted through the engine exhaust gases as well as by evaporation from gasoline tanks and carburetors and in gasoline handling operations in general. Exhaust products from diesel engines are similar in type to those from automobiles but vary significantly in the relative amounts of the various components.

From extensive research and experimentation by several investigators, notably Los Angeles County Air Pollution Control District, Stanford Research Institute, and the automobile industry, has emerged extensive data on the composition of exhaust gases from internal combustion and diesel engines in terms of the relative amounts of each of the major components. This information is reported in terms of weight of exhaust component per unit volume of gasoline or diesel oil consumed. Thus it is possible to calculate the emissions from automobiles, trucks, and busses in a given area from information on the volume of the respective motor fuels consumed in that area. Emissions from locomotives powered by gasoline and diesel oil may be estimated. as in the case of motor vehicles. Using a procedure developed by the American Petroleum Institute and the Los Angeles County Air Pollution Control District it is possible to calculate the hydrocarbon losses from gasoline storage tanks.

Steam-operated locomotives and vessels constitute another, although gradually diminishing, source of pollution from transportation. The emission rates of flyash and sulphur dioxide can be calculated from available figures of tonnage and composition of coal and fuel oil used, with due consideration to combustion equipment and practices.

Combustion of Fuels for Heat and Power

The burning of fuels for the production of power and hot water, heating of homes, apartments, public and private buildings, represents an important source of air pollution. The emissions from this source may be estimated by calculations based on the rates of consumption of fuel oil, manufactured and natural gas, coal and wood. Fuel consumption figures may be obtained from the American Petroleum Institute, Bureau of Mines, public utilities, and local fuel distributors.

The products of combustion of fuel oil, gas and coal include oxides of sulphur and nitrogen, hydrogen sulfide, hydrogen cyanide, formaldehyde, organics, fluorides, acids and aerosols in varying amounts depending on the particular fuel. Applying data on the relative amounts of these emissions to the individual rates of fuel consumption, it is possible to calculate the daily emission rates of each component in such terms as tons produced/ton of each type of fuel burned.

Incineration of Solid Wastes

The incineration of wastes produces gaseous and particulate emissions which are significant in terms of quantities as well as potential importance in producing undesirable air pollution. The pollutants from waste burning include organics, aerosols, aldehydes, ammonia, acids, and oxides of sulphur and of nitrogen. By combining known or estimated emission rates for municipal, commercial, backyard and wood-waste incinerators and burning dumps with data furnished by local authorities on the relative quantities of wastes burned in the various types of incinerators, it is possible to estimate the total emission rates of the various pollutants.

Production of Solvent Vapors

Solvent vapors emitted from a large variety of domestic, commercial, and industrial operations represent a considerable source of significant air pollutants. Such operations as dry cleaning, painting and degreasing are typical of activities responsible for the evaporation of solvents. Emission rates may be estimated on the basis of quantities of solvents consumed or paint used in a given area. Such figures may be obtained from local distributors of these materials.

Miscellaneous Odor-Producing Activities

For the sake of completeness, an emission inventory should include a tabulation of sources giving rise to objectionable odors. Odors per se are not readily categorized according to their chemical composition, nevertheless information on the number and types of odor-producing activities is extremely useful in a community air pollution study. This list may include sewage and industrial waste treatment plants, stockyards, hog farms, as well as certain other industrial and agricultural activities producing malodors.

Specific Source Inventory

Industrial plants comprise a category of air pollution sources presenting the widest range in quantities and types of air pollutants. Individually and collectively they represent a complex chemical system which, from an emission inventory standpoint, are most effectively treated directly on an individual basis. The Specific Source Inventory of a community has as its objective an evaluation of each major industrial source in that area. In the Special Air Pollution Study in Louisville, the procedures and techniques employed in each plant studied are as follows:

(1.) Initial Contact

An initial contact with industrial management, preferably a visit, allows an opportunity to explain the major purpose of the survey and specific objectives sought. It gives management an opportunity to become fully acquainted with activities to be scheduled in the plant. This procedure leads to a friendly basis of understanding and, in our own experience, to strong cooperation without which subsequent efforts would have been much more difficult, if not impossible in some instances. Where distrust or doubt can develop regarding motives and methods, confidence and good will may instead be established. This is particularly important later in the general acceptance of the findings which are made.

(2.) Preliminary Survey

The next important step in industrial source inventory methods is the preliminary survey. This is a brief but intent look at all of the factors which determine the type and extent of planning to be done prior to actual measurements or sample collection. While the procedures involved in this step should be as simple as possible, the actual amount of effort required, naturally depends on the nature of the emissions and the complexity of operations or processes producing them. The activities included in the preliminary survey broadly include: *(a)* briefing by management on processes and operations which contribute to emissions; *(b)* thorough physical inspection of these processes and operations and of the points of emission and *(c)* estimation by material balance or calculated values volunteered by management, on the types and quantities of effluents suspected of escaping into the atmosphere. These efforts may require anywhere from a day to a week, but are well worth the time.

Familiarity with processes and operations provides qualitative information on the nature of the effluents, such as their physical status, whether they are gases or particulates, hot or cool, wet or dry, released at atmospheric or at elevated pressures, *etc.* A simple flow diagram spotting the points of emission and indicating the details just referred to, serves as an excellent reference to be used in the guided physical inspection tour which follows.

A management representative conducts the tour and provides requested information. As each emission point is viewed, data regarding its physical location, accessibility, the availability of electrical power, the presence of safety hazards, the type and size of emission stacks or other venting equipment, the frequency and duration of venting and their relationships to operational cycles are all noted. Observing the effluents where possible, and even smelling or feeling them may provide useful information. Armed with the facts obtained from the process briefing and the inspection tour, significant points may be singled out to perform some preliminary calculations on the expected magnitude of stack velocities, *etc.* One may become good enough at this to reduce the number of samples required or measurements taken, but great care should be exercised in substituting such data for actual determinations.

(3.) Preparation

Proper regard for the preliminary survey will surely produce enough background information to allow ade-

TABLE I

Source Sampling Schedule

Source	Measurements		Dust Sampling					Gas Sampling %			
			Dust Loadings		Millipore Samples		Hi-Vol Samples (% Comp.)				
	Gas Flow Rate ($Ft.^3$/ Min.)	Temp. of.	Gr./$Ft.^3$	Lb./Hr.	Particle Size Frequency Analysis	Spectro-Graphic and X-Ray Diffraction (% Comp.)		H_2O	CO_2	SO_2	SO_3
Stack #1 — 60′	X	X	X	X	X	X		X	X	X	X
Stack #1 — 160′	X	X	X	X	X	X		X	X	X	X
Stacks #2 Lime Kiln	X	X	X	X	X	X		X	X	X	X
Stacks #3 & #4 Coke Drier	X	X	X	X	X	X		X	X		
Stacks #5 through #10	X	X	X	X	X	X			X		
Roof Escape	X		X	X	X	X	X		X		

quate preparation for emission inventorying.

An obvious sequence in preparation is to decide on *(a)* what information needs to be ascertained, *(b)* what methodology is required, *(c)* how much and what type of equipment is needed, *(d)* the number and types of personnel required, and *(e)* a sampling and measurements schedule.

(4.) Sampling and Measurement— Particulate

Sampling and measurements are the next consideration. The number of methods is rapidly growing and adaptations become more numerous as new problems are encountered. Without attempting an exhaustive presentation of all published methods, some which have been successfully employed on the Louisville Study will be discussed.

The techniques used in determining particulate emissions can best be described by referring to the procedure actually employed at an industrial plant generating dust and fumes. This particular source study (Table I) was conducted in cooperation with technical personnel from the U. S. Bureau of Mines using equipment developed or modified by them.

Gas flow rates were determined for each stack source by the use of a type *S* Pitot tube, and the temperature was measured with an integral thermocouple (Fig. 1). Gas flow rates from roof openings were determined by measurement with a Velometer. Temperature measurements were made with a mercury thermometer. Moisture content in stacks was determined by a hygrometer, and checked by measuring the amount of condensate collected during dust sampling. The integrated traverse method was used in all stack measurements (Fig. 2 and 3).

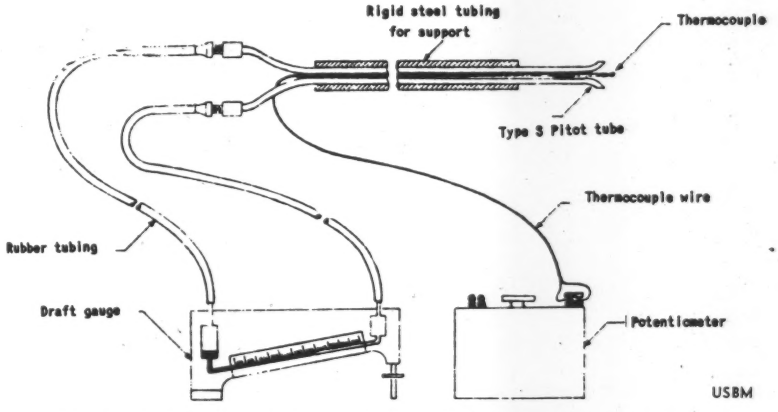


Fig. 1. Equipment for stack gas velocity and temperature measurements.

Dust loading samples were obtained from each stack on Whatman 43 x 123 mm. double-thickness paper thimbles. The procedure employed is a modification of Western Precipitation Corporation procedure (Fig. 4 and 5). At roof openings, dust loading samples were taken with either a high volume sampler using type *S* filters, or an electrostatic precipitator.

Size frequency analyses of dust in the stacks were made on samples collected on Millipore filters, type AA, 47 mm. diam. disks, held in a standard aerosol filter holder modified so that the entire unit could be inserted in the stack (Fig. 6). To accomplish this, the holder was fitted to various lengths of ½ in. I.P.S. stainless steel pipe and provided with a curved nozzle and a limiting orifice. Millipore samples were taken during time intervals varying from 1/5 sec. to 10 min. Deeply stained millipore disks may be used when sampling white dusts to make counting easier. Particles do not drop off the filters unless they are unusually large. The uniformity of particle concentration across the filter is good except when the stack contains water droplets. Very few agglomerates were observed. To count the finest particles, microscope immersion oil was used to make the filter invisible.

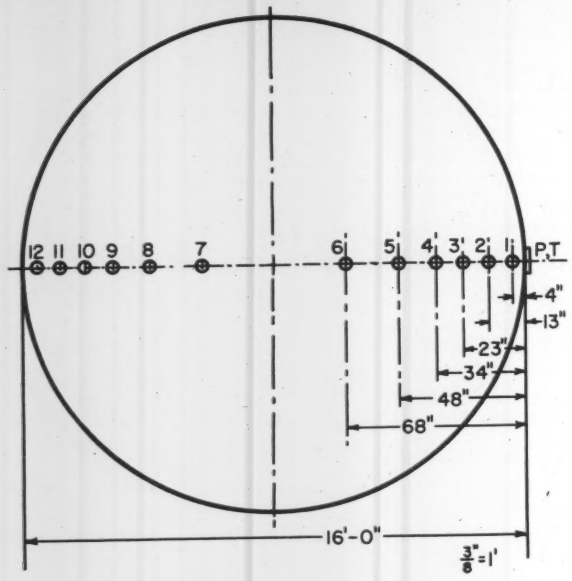


Fig. 2. Pitot tube traverse layout. Note: Points P-1, P-2, etc., are at the 60' level. Points T-1, T-2, etc., are at the 160' level.

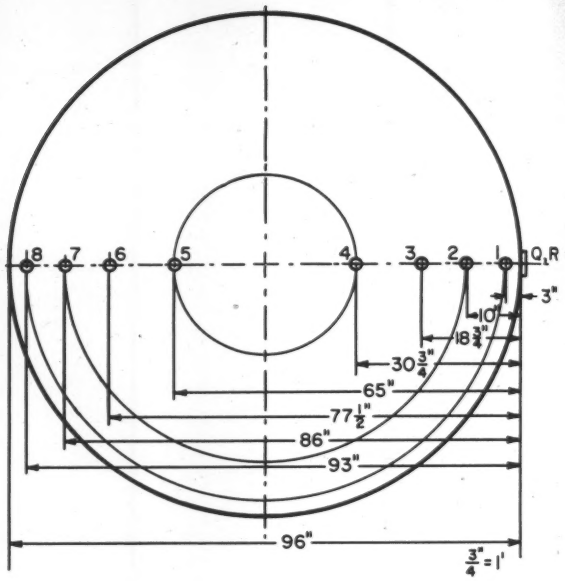


Fig. 3. Pitot tube traverse layout. Note: Points Q-1, Q-2, etc., are for Stack No. 2. Points R-1, R-2, etc., are for Stack No. 7.

It is felt that this is an effective method for the determination of the types, quantities, and characteristics of emissions from this plant. This opinion is further supported by the fact that a comparison of results at this plant checked remarkably well with data collected by management by independent tests.

(5.) Sampling and Measurement—Gases

Gas sampling methods employed on the Louisville Study were developed to accommodate specific requirements encountered in industrial sources. One method which proved to be highly successful is the one developed by Brief and Drinker. This method (Fig. 7) is applicable to the collection of effluents produced by both cyclic and continuous operations where pollutants are discharged to the atmosphere through vents or stacks. The collection apparatus which comes in contact with the sample is constructed of glass throughout. It consists of an open-end mercury manometer, a 2-*l.* grad flask surmounted by a manifold, a vacuum connector, a flushing piece, and a sampling probe. The manometer, the flask with manifold and the vacuum connector are assembled. The system is evacuated to below 1 mm. Hg. The vacuum connector is replaced with a sampling probe with a flushing *T*. The probe is first flushed with stack effluent. Purging is stopped and gases are let into the flask through valve *A* at a constant rate.

The amount of gas sampled is related to the rise in pressure in the flask as indicated by the manometer. The flow rate is controlled by the valve *A* which represents 2 orifices in series. If the gas sampled approximates air at 1 atm. pressure, constant flow is maintained across this stopcock until the flask pressure reaches 0.39 atm. This is the critical pressure ratio. Above this pressure in the flask, the flow rate must be maintained by adjustment of the stopcock. Advantages of this method are that the equipment is relatively inexpensive, light, and simple to use. Of great importance is the fact that the collected sample is easily transported to a distant point for analysis. This method lends itself equally well to short period or extended period sampling. The integrity of the sample is well maintained and transfer of the sample is uncomplicated.

A technique developed on the Louisville Study, especially for sampling gases exhausted through steam jets, employs the freeze-out principle. This method (Fig. 8), consists of bringing the sample through a condenser where all moisture is removed. The remaining gases pass into a liquid nitrogen-cooled freeze-out trap where they are condensed or frozen. Non-condensible gases, which should be of little interest from a pollution standpoint, are drawn through the system and exhausted through the vacuum pump. Pressure drop is regulated with the bleeder arrangement. This method offers the advantage of allowing the collection of gas from a stream of dry steam over any time period required, continuously or intermittently as desired.

Flow rate control is achieved by utilization of the pressure drop prin-

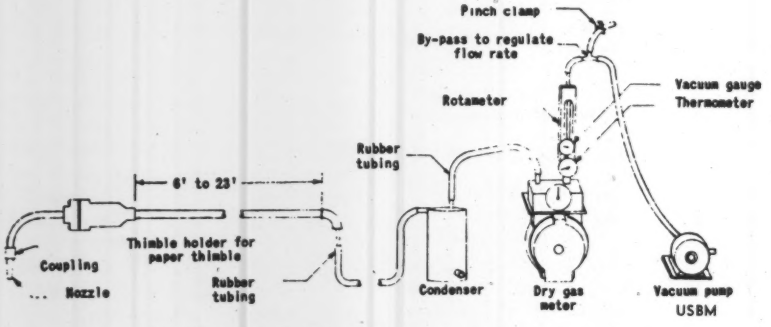


Fig. 4. Equipment for measuring dust concentration in stack gas.

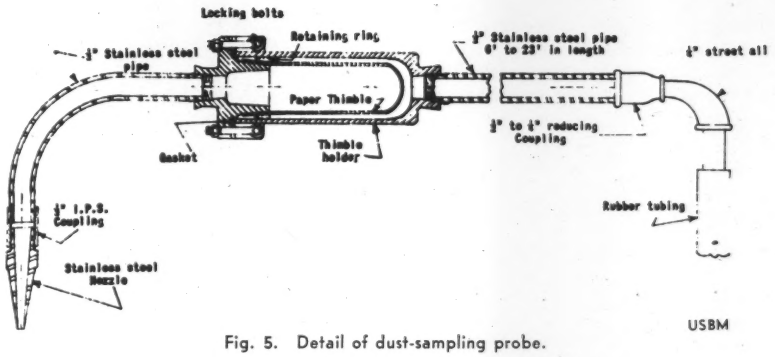


Fig. 5. Detail of dust-sampling probe.

ciple mentioned in the grab sampling technique above. The amount of moisture collected for a definite time period in the condenser is either measured or weighed. The rate of emission from the jet is then determined by calculation. The pounds of steam released through the jet is a constant depending on the steam quality, quantity, and pressure at the inlet of the jet. The rate of collection is compared to the total emission rate. The quantity of pollutants collected bears the same relationship to the total quantity emitted, (Fig. 9).

Samples collected by these two procedures may be subjected to any of the standard instrumental, physical, and chemical methods required. Most of the grab and freeze-out samples collected on the Louisville Study have been analyzed by Mass Spectrometry at the National Bureau of Standards.

Emission Estimates Based on Waste Liquor Losses

Another method of source sampling involves the determination of gaseous pollutants escaping in waste liquors either as volatiles present in the waste or those that result from chemical reactions in subsequent handling. As a case in point, consider the production of acetylene from crushed calcium carbide. Spent carbide leaving the generator may contain unreacted material which, upon subsequent handling and disposal, exposes fresh carbide to the waste liquors to to atmospheric moisture. Acetylene thus generated escapes and contributes to air pollution. Some acetylene gas is absorbed in the water as it leaves the generator. A sample of the liquor may be obtained in an evacuated flask and the dissolved gases determined. A sample of the solid material coming out of the generator on the other hand may be treated in the laboratory to complete the reaction of the carbide to determine how much additional acetylene may be generated under ideal conditions. Using a definite quantity of sample in such tests, permits calculations of potential acetylene losses based on total quantities of such wastes discharged.

Emission Estimates Based on Evaporation Losses

The next source sampling method of interest is that used in determining losses of volatiles in an industrial operation treating wooden cross-ties for railroads. At this plant thousands of ties are creosoted and stored in the open, for a period of a year or more. The escape of volatiles to the atmosphere contributes to the air pollution.

In the approach used on the Louisville Study, borings are taken from ties which have been exposed to the atmosphere for varying lengths of time so that losses can be computed for different aging periods. Borings of a given aging period are steamed

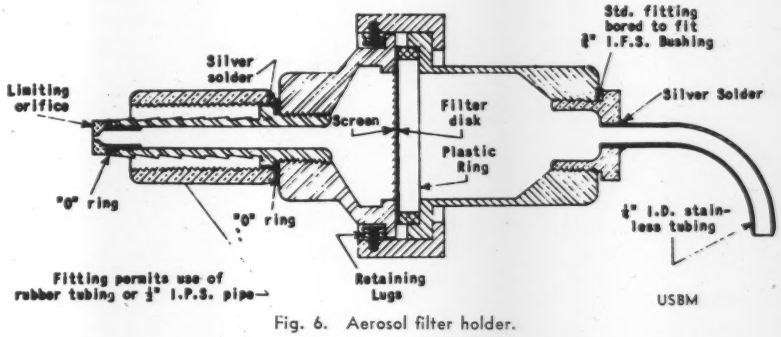


Fig. 6. Aerosol filter holder.

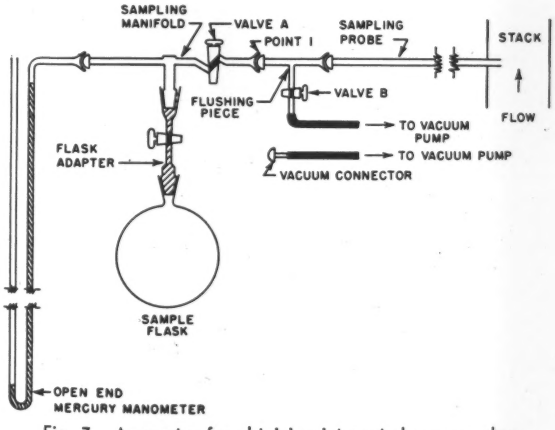


Fig. 7. Apparatus for obtaining integrated gas samples.

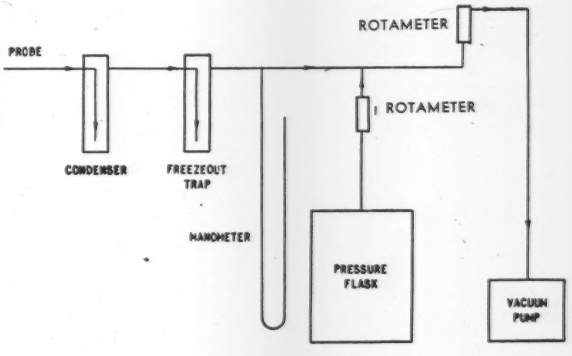


Fig. 8. Steam jet sampler assembly (Schematic).

to remove the volatiles which may then be analyzed by mass spectrometry. Knowledge of the number of ties processed and the average time of exposure permits calculation of losses.

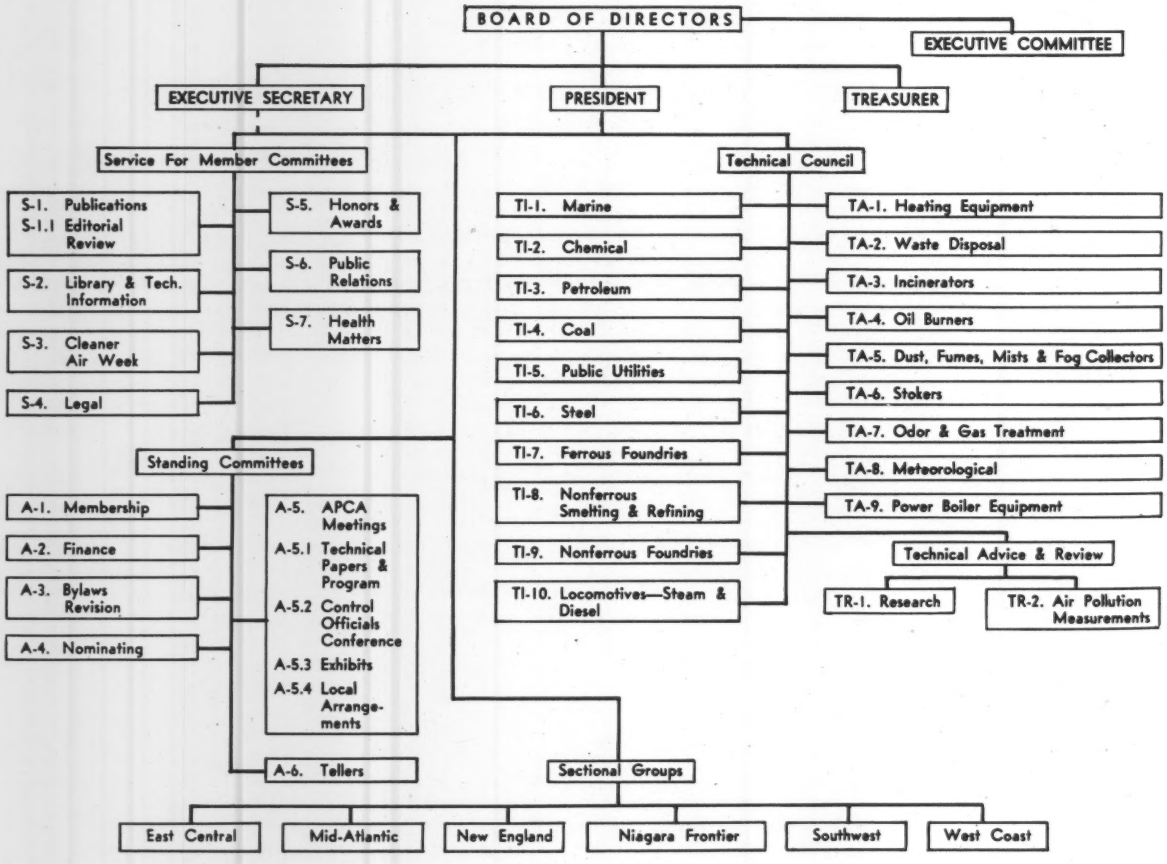
Conclusion

In summary, it is again emphasized that the approach employed in making an emission inventory is a function of the particular air pollution problem under investigation. A reasonably accurate estimate of emissions from multiple sources such as transportation, heat and power production and waste incineration can be made on the basis of such available figures as quantities of fuel and wastes burned in conjunction with knowledge of products of combustion. In the case of specific source studies, although standard procedures have been established for some types of sampling, modifications are often necessary. While the few examples mentioned here will by no means suffice for specific sampling problems which are bound to occur, they may serve as a guide in developing the appropriate approach.

References

1. August T. Rossano, Jr.. The Joint City, County, State, and Federal Study of Air Pollution in Louisville, Kentucky. *Journal of Air Pollution Control Association* **6**, 3:176-181. November 1956. (Also published as The Louisville Study). Public Health Reports. 72:67-70. January 1957.
2. Evaporation Loss of Petroleum from Storage Tanks. *Proceedings 32nd Annual Meeting of the American Petroleum Institute*, Chicago, Illinois, November 1952.
3. Literature Review of Metropolitan Air Pollutant Concentrations." Stanford Research Institute, November 30, 1956.
4. Investigation of Air Pollution in the Vicinity of Portland, Oregon. Stanford Research Institute, October 4, 1956.
5. Roy O. McCaldin, and Paul A. Kenline, Air Pollution in Connecticut. State of Connecticut and Public Health Service, Robert A. Taft Sanitary Engineering Center, September 1956. 111 pp.
6. E. R. Hendrickson, D. M. Keagy, and R. L. Stockman. Evaluation of Air Pollution, State of Washington. State of Washington and Public Health Service, Robert A. Taft Sanitary Engineering Center, December 1956. Mimeo. 145 pp.
7. Discharge from Municipal Incinerators, *Air Repair* **3**, 2, November, 1953.
8. R. S. Brief, and P. A. Drinker. Collection of integrated samples of gaseous effluents. *A.M.A. Arch. of Ind. Health*, **17**, 654-8, (June 1958).

How Your APCA Is Organized



Methodology for Evaluating the Air Pollution Problems of A State

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Realizing that pollution of the atmosphere by domestic, industrial and agricultural activities is becoming an ever-increasing environmental problem, some states have recognized the need to assess their current and potential air pollution problems in order to inaugurate prevention and control activities without delay. In some instances, states have sought the assistance of the Federal Government which is available and which has been offered through the program established by Public Law 159 of the 84th Congress. This program is being administered by the Public Health Service.

The methods described here were developed and used in four state-wide air pollution appraisals in Connecticut, Washington, Tennessee, and Texas during the past two years and will shortly be put to use in a fifth such study in North Carolina. All five studies have been, or in the case of North Carolina will be, cooperative studies conducted jointly by members of the staffs of the state health departments and the State and Community Services Section, Community Air Pollution Program, Public Health Service.

The objective of a state-wide appraisal should be to assess present and potential air pollution problems and to secure data from which the state can determine the need and scope of a future program or activity.

The scope of a state-wide appraisal can range anywhere from a brief reconnaissance based on visual observations to a detailed study including air sampling and analysis extending over a period of several years. The methodology herein reported is intermediate between these two approaches in that it does not include air sampling and analysis but extensively and intensively exploits all existent data in the state relevant to the air pollution problem. Until detailed information is obtained relative to existing sources and the compounds which may be involved in the emissions therefrom, it is nearly impossible to know the pollutants for which one should sample. The procedures which have proven useful in obtaining this data have included questionnaires, interviews, visual observation, review of material in libraries and office files, estimation, and computation based thereon. This approach required about one man-year of effort for each of the four state studies mentioned earlier. Such a study can be a one-man operation but preferably it should have a minimum of two men and a secretary.

It is almost impossible to set forth a time table which would be adaptable to any state-wide survey. There are many variables and considerations. However, there are four distinct, time-consuming phases of a study of this type which should be noted:

(1) The *arranging-for-the-study* phase. This is the period when the cooperating agencies or persons communicate, formally or informally, and make the necessary arrangements for personnel, policy, money and facilities.

(2) The *orientation-of-the-investigators* phase. The length of time needed for this phase is of course dependent upon the investigators' knowledge of, and familiarity with, the state and the problem.

(3) The *gathering-the-information* phase. Proximity to the sources of information and the number of cities to be visited are probably the principal factors in the length of time required for this phase.

(4) The *report-writing* phase. It is assumed that study and analysis of the data will be done during the course of these latter two phases and, therefore, report writing is not a distinct part of the time table. Two factors greatly affect the time required: the amount of review and clearance required, and the form of the final report.

Types of Data Needed

Since all state surveys to date have involved health departments, it has been necessary first to agree that, despite the usual limitation of health department activity to that which directly affects public health (as interpreted in its broadest sense), an air pollution appraisal to be of any real value must embrace an even wider area of interest. It must explore the effect of air pollution which has been defined as the presence in the atmosphere of substances, put there by the acts of man, in concentrations sufficient to interfere with his comfort, safety, and health

or with the full use and enjoyment of his property. This definition was used in the recent studies and is widely accepted today. It recognizes the need for inclusion in the appraisal of studies of plant, livestock and material damage, studies of problems associated with visibility reduction, and problems associated with non-disease-producing attacks of air contaminants on our senses and our attitudes. It further recognizes that the atmosphere is self-cleaning and that a certain amount of impurity in the air can be tolerated without the creation of an air pollution problem.

The types of data needed for assessing *past* and *current* problems, therefore, include:

- Complaints by the public
- Evidence of damage
- Results of sampling activities
- Opinions and experiences of individuals
- Emission data
- Climatological and meteorological data and analyses

For estimating the potential problem, additional information is needed on:

- Population density and growth trends
- Industrial density and growth trends
- Fuel use patterns and trends
- Topographical data and maps
- Refuse disposal practices
- Agricultural practices
- Transportation data

STATE OF WASHINGTON DEPARTMENT OF HEALTH
AIR POLLUTION SURVEY QUESTIONNAIRE

July 23, 1956

Please check the appropriate box and provide information for any YES answer briefly on the reverse side or attached sheet.

	YES	NO
1. Are there *any* operations (municipal, domestic, industrial) in or near your area of jurisdiction that emit noticeable amounts of smoke, fumes, dust, or odor to the atmosphere?	( )	( )
2. In your opinion, are the smoke or other pollutants in sufficient concentration to cause:		
a. Measurable discomfort or inconvenience to residents?	( )	( )
b. Damage to property? (autos, paint, clothing, buildings, etc.)	( )	( )
c. Damage to vegetation? (lawns, crops, flowers, etc.)	( )	( )
3. Have you received complaints of air pollution in which the complainant claims:		
a. Noticeable discomfort or inconvenience?	( )	( )
b. Damage to property?	( )	( )
c. Damage to vegetation?	( )	( )
4. Do any of the problems result from seasonal activities?	( )	( )
5. Are any of the problems the result of seasonal or periodic weather conditions?	( )	( )
6. Are there any local ordinances or regulations for the control of smoke, fumes, dust and odor?	( )	( )
7. Do you know of any activities planned for the future in your area which might contribute to air pollution?	( )	( )
8. Have any steps been taken to assess the local air pollution situation such as surveys, inspections, or investigation of complaints?	( )	( )
9. Are there any other groups (official or unofficial) in your community who might furnish additional information regarding air pollution problems?	( )	( )

Name of individual reporting _____

Name of (fill in one)
City _____
County _____
District _____

Return to: Washington State Health Department, Engineering Division, Smith Tower, Seattle 4, Washington.

Fig. 1

The need for data on the emission rates of all types of pollution-causing activities and processes has been recognized, and attention is being directed toward the difficult problem of obtaining the information. It was only partially obtained during the initial surveys,[1,2,3,4] but it is hoped that more comprehensive emission estimates can be made in current and future studies.

The need for information on climatology and topography is apparent; these are the natural factors affecting the pollution potential of any area. Data on trends regarding population and industrial growth, fuel usage, refuse disposal practices, and transportation practices are significant with respect to the wastes discharged to the atmosphere because they allow us to estimate the degree of the potential problem.

Information regarding agricultural practices and experiences is needed not only for the purpose of estimating economic damage received and caused, but also for possible valuable data that might be found regarding plants as indicators of pollution.

Sources of Data

A list of the possible sources of information and data would be too lengthy for inclusion in this brief report. However, the following list gives some of the information sources found useful in the surveys made thus far:

1. Official and private agencies
2. Public and private officials
3. Published and unpublished data and analyses
4. Field visits by the investigators

Gathering the Information and Data

The complaint records of official agencies constitute one of the first places to look for information as to whether or not the public has recognized air pollution as a problem. Records of complaints regarding nuisances from smoke, dust, odor, *etc.*, or regarding damage to plants, animals, paint, *etc.*, may be found in a number of offices. They are submitted to the mayor or city manager, the city council, the health department, the city clerk, the building department, the police or fire departments, the public works department, the county agricultural agent, and un-

doubtedly there are records of complaints on file in other offices. For the State as a whole, complaints are usually filed with the state health department.

If there is no formal air pollution program in the area, action taken on the complaints ranges anywhere from filing them in the waste basket to forwarding them to designated departments or persons for investigation and any action possible under existing laws, ordinances, or regulations.

It is to be noted that the number of complaints filed is not necessarily a measure of the extent or degree of pollution. The number received may be influenced by, among other factors, the attention given to previous complaints, or by the nature of the pollution with respect to whether it is a chronic condition or an acute situation. The public may have learned to live with a chronic condition, but on the other hand, it may flood the city hall with complaints regarding a less serious nuisance which persisted for only a few hours. An examination of complaints will usually reveal which of these two types of pollution was encountered. This knowledge will then serve as a guide to the investigator as to the procedure to follow in his assessment of the air pollution problem of the area.

Another available source of information as to the existence of a recognized problem are the state or local officials themselves. This is especially true where chronic conditions exist for which there are no written complaints on file. Local officials are usually aware of these situations through personal observation or through the receipt of verbal complaints from citizens or groups. The mayor or city manager, the city or county engineer, the local or state health officer or any of his professional staff of engineers, sanitarians and nurses, or the city or county planner are some of the best possible sources of such information. Again, however, discretion and care must be used in interpreting the findings. In addition to the factors affecting the reliability of recorded complaints, is the possibility that the official may be biased in the matter. In one of the cities studied, the only complaint found was that of a city councilman whose store and home on the outskirts of the city were the only dwellings in the prevailing path of a smoke plume from a factory chimney.

STATE OF TENNESSEE
DEPARTMENT OF PUBLIC HEALTH

Air Pollution Appraisal Questionnaire

	YES	NO
1. Are there any operations (municipal, domestic, industrial) in your area of jurisdiction that emit objectionable amounts of smoke, fumes, dust or odor to the atmosphere?	( )	( )
2. In your opinion are these pollutants present in sufficient concentrations to cause:		
a. Discomfort or inconvenience to residents?	( )	( )
b. Damage to property? (autos, paint, clothing, buildings, etc.)	( )	( )
c. Damage to vegetation?	( )	( )
d. Injury to animal life?	( )	( )
3. Has your office received complaints concerning air pollution during the past two years?	( )	( )
4. Are the air pollution problems in your area of jurisdiction principally due to:		
a. Municipal activities (dumps, incinerators, etc.)	( )	( )
b. Domestic activities (incinerators, heating plants, etc.)	( )	( )
c. Commercial activities?	( )	( )
d. Industrial activities?	( )	( )

5. Please describe briefly any air pollution problems in your area of jurisdiction.

6. In your opinion is the problem described above of major ( ) or of minor ( ) significance?

7. Are there any local ordinances or regulations for the control of smoke, fumes, dust or odor?	( )	( )
8. Have any steps been taken in your area of jurisdiction to control sources of air pollution?	( )	( )
9. Are there sources of air pollution outside your area of jurisdiction which have created a problem in your area?	( )	( )

10. Please list any other groups (official or unofficial) in your area of justdiction who might furnish additional information regarding air pollution problems.

Return to: Industrial Hygiene Services, Tennessee Department of Public Health, Nashville, Tennessee.

County:

Signed: _____

Fig. 2

The remaining sources of information may be grouped under the broad heading of published and unpublished data on all factors of air pollution. These publications may be public or private and are to be found in such places as the offices of local, state and federal official agencies; in the files of industry and private associations; in the offices and libraries of universities and other research agencies; and in miscellaneous places such as the Chamber of Commerce, the bank, the public library, and the utility companies.

At first glance this gathering of data may seem to be an overwhelming task. Admittedly it is time-consuming to locate and procure these many publications and reports and to glean the desired information from them, but with the knowledge of the type of information being sought, the investigator will find the task by no means endless or frustrating.

Usually it is quite obvious where the information can be found. Population information is available at the local office of the Bureau of the Census and chambers of commerce and universities may also provide pertinent data. The local or state fuel dealer's association is a primary source of information on fuel usage. For meteorological and climatological data, the local Weather Bureau offices are the obvious choice. A search for published or mimeographed reports in regular or office libraries will disclose much information relative to the number and type of studies which have previously been made; university libraries are usually a good starting point. Questionnaires and interviews may reveal the existence and location of these reports. Very often records of air sampling are a part of the study reports. Dust fall records, sulfur dioxide concentrations, fluoride concentrations, and filter tape data are often available.

In discussing the methods of obtaining the data, the importance of making early contact with and visits to the agencies and associations which might contribute materially to the success of the study cannot be overemphasized. Such agencies will appreciate an explanation of the purpose, objectives and scope of the study and will usually reward the investigator with their fullest cooperation.

The initial data-gathering activity may well be the designing and mailing of the questionnaire. Questionnaires serve several purposes in addition to the principal one of collecting information and data. When mailed early, they provide information which materially assists in planning or modifying the conduct of the study and they pave the way for later interviews when there are gaps to be filled. They arouse and foster interest in the subject of air pollution. Examples of questionnaires (Fig. 1 and 2) used in the several state studies show, without further explanation, the kinds of questions asked and the method of asking them. They should be sent under a transmittal letter from the state health officer, his representative or some such person of authority in the state (Fig. 3). The letter should relate the objective and scope of the study and should clearly indicate how the information is to be used. The party receiving the questionnaire thus feels that his information is needed and will be inclined to furnish more complete answers.

STATE OF WASHINGTON

DEPARTMENT OF HEALTH

DIVISION OF
ENGINEERING AND SANITATION

SMITH TOWER

SEATTLE 4

September 10, 1956

To The Management
Manufacturing and Process Industries
State of Washington

Subject: Air Pollution

Dear Sir:

There has been considerable interest shown over the past few years regarding present and potential air pollution problems. The attached Health Department "Statement" explains a study now underway, the purpose of which is to bring into better perspective the actual situation on a state-wide and local or regional basis. It is a fact-finding study and, as indicated in the 'Statement', will provide a foundation for the determination of the need for and type of future activity.

Your knowledge and information about your own particular installation can be most helpful and is most essential to us. Accurate industry information is needed so that this source may be placed in its proper perspective in relation to other sources including transportation, domestic activity, agricultural practices, refuse disposal, natural sources, etc. The attached "Industrial Questionnaire" is designed to obtain general information by areas and communities as to types and sizes of industries and the control activities already accomplished. The information obtained will not be reported in detail nor referenced to a specific industrial installation by name.

We urgently request your co-operation in completing the questionnaire and returning it at your earliest convenience. Please feel free to supply such additional information or comments as you may desire.

Your interest and co-operation will be greatly appreciated.

Yours very truly,

ROBERT L. STOCKMAN
Engineer in Charge
Air Pollution Program

Fig. 3.

Information secured through the use of the questionnaire must be interpreted with recognition of certain limitations. These include: the degree of objectivity of the questionnaire, the informativeness or bias of the answers, the degree of coverage, and the percentage of questionnaires returned.

Field visits may be initiated as soon as the questionnaires have been mailed. Interviews should, of course, be arranged by appointment and should be brief. Repetitive interviews such as with health officers, city engineers, *etc.*, should be standardized for thorough and efficient analysis of answers. A check sheet or interview data sheet will serve this purpose. The one used during the Connecticut study (Fig. 4) is self-explanatory.

These interviews have proven productive and valuable in many re-

spects. Among other things, they assure the public that this is not a swivel-chair survey; like the questionnaires, they foster or arouse interest in the subject; they provide information which fills in the gaps between the questionnaires, the studies, and the published reports; and they provide leads to additional sources such as informed persons or offices and obscure published or unpublished studies and reports.

Visits to representative areas and to selected locations of special interest complete the list of methods for obtaining information. Firsthand observation by the investigator is a "must" where time and travel permit. Although recorded and verbal complaints will probably bring to light many past problems and nearly all present ones, it is probable that the trained eye of the investigator will detect additional conditions or circumstances worthy of note. Furthermore, it should be recognized that the reader of the final report will be inclined to discount its validity if it is known that the report was written without the author having personally witnessed present emissions or existing damage. Field trips should be so planned that all principal cities and nearly all counties are visited. In the Washington and Tennessee studies the investigators went to all cities of over 10,000 population and to all other communities where a questionnaire return or other source of information indicated existence of an air pollution problem. In Connecticut all cities of over 20,000 were visited. In Washington, trips were scheduled to the county seats of those counties omitted by this procedure.

INTERVIEW DATA SHEET — PART I

AIR POLLUTION SURVEY
CONNECTICUT STATE DEPARTMENT OF HEALTH
MAY 1956

Town: _____
Persons Interviewed: _____
_____
Date: _____

I. Town description:

1. Estimated population (July 1, 1956) _____
2. Labor force (June 1955) _____
3. Number of manufacturing employees (June 1955) _____
4. Predominant industry _____; number of employees _____
5. Topography _____

II. Remedial action:

1. Legal controls

(a) Air pollution control ordinance: yes _____ no _____

(b) Air pollution control provisions in:

Zoning ordinance:	yes _____	no _____	Ordinance not examined _____
Heating ordinance:	yes _____	no _____	Ordinance not examined _____
Incinerator ordinance:	yes _____	no _____	Ordinance not examined _____
Pollen control:	yes _____	no _____	Ordinance not examined _____
Nuisance regulations:	yes _____	no _____	Ordinance not examined _____

2. Activity

(a) Studies or surveys: date _____ by _____
(b) Complaints received: Number/year _____, none _____
(c) Problems investigated by: H.D., F.D., B.D. _____, none _____
(d) Problems investigated by: S.H.D. _____
(e) Time on air pollution: (man months per year) _____

Fig. 4

Results Expected

Despite the fact that no sampling of the ambient air or emission sources is made during the course of the survey, a qualitative determination of the existence and severity of air pollution in the state can be made. Samples are not needed to show that a problem exists if one can observe a pollution pall hanging over a city. The local citizen does not need air sampling data to tell him that visibility is reduced, that his eyes smart, and his clothes get dirty hanging on the line. Maybe he doesn't know the exact element or compound involved, but he does know that he is experiencing the effects of air pollution. He may suspect that "something in the air" is causing damage to his plants and to the finish on his automobile, but extensive, detailed sampling may be required to prove it. If the condition has been serious enough for a relatively long period, a special study of the problem may have been conducted and the results noted during the course of the state-wide survey. Thus, a survey of this type should discover suspected air pollution problems and the final report should indicate the need for further investigation.

In addition to results which point to obvious and suspected air pollution problems, analysis of the information collected will permit delineation of the geographical distribution of the problem areas. For instance, until it is noted that five cities for example, are influenced by common meteorological and topographical conditions, it may not be recognized that on some days the bulk of the pollution from all five cities is concentrated over one of them. An analysis of these natural factors, along with such factors as population growth and density, fuel usage, *etc.*, permits sounder judgment as to where pollution may be a problem in the the near or distant future.

Survey results may be used in several ways. First, they should be used in the manner intended — to serve as a guide to future state action. Since the investigator should be able to conclude whether air pollution is the cause, or the suspected cause of a problem in specified geographical areas or fields of interest, his con-

INTERVIEW DATA SHEET — PART II

III. Problem evaluation

Source of Air Pollution	No. of Prob.	Severity of Problem			Type of Pollution				Heat. Plant	Incin-erator	Sources in other municipalities
		Major	Minor	Neg.	Smoke	Dust	Odor	Fumes			
Total											
Private Homes											
Apartments											
Hotels											
Office Bldg.											
Store											
Bakery											
Laundry											
School											
Hospital											
Incinerator											
Dump											
Vehicle exhaust											
Utility											
INDUSTRY:											
Textile											
Lumber & furn.											
Paper											
Chemical											
Drugs											
Petroleum & Coal											
Rubber											
Leather											
Stone, clay, glass											
Primary metal											
Fabricated metal											
Mining											
Miscellaneous											

Fig. 4(Cont'd.)

clusions should result in recommendations for prevention, control, or further detailed study.

Any picture of the state situation is a composite of reports on local conditions. Survey results, therefore, should next serve as an assessment and guide not only for state officials but also for local and regional officials. One of the principal observations which such officials can make, is to emphasize the adequacy of, or the need for, control regulations. Adequacy, in this context, must be specified in terms of the measures used in the appraisal rather than in terms of gravimetric or volumetric air analysis.

Finally, one of the most rewarding results of the survey is the fact that it serves as a starting point for any future program or activity which may be initiated. If a representative of the state assists in, or alone conducts the investigation, he becomes familiar with the science of air pollution prevention and control and gains first-hand knowledge of the status and potential of air pollution problems of his state. He will secure much valuable information and data which, although they may not appear in the report, may serve as useful reference or evaluation material at a later date. The results of a survey, then, serve as a guide to state and local officials, as a sound starting point for an active program, and as a base line for future evaluation of

the air pollution problems or program of the state.

It is increasingly evident that air pollution problems are experienced wherever there is industrialization and urbanization. Hardly any of the forty-eight states can disclaim a current or potential pollution problem in some area of that state. Therefore, it would seem that each state must eventually make a preliminary assessment of its air pollution situation. It is recognized that each state must tailor its own survey to its particular need and circumstances. However, the methods discussed here should prove useful in planning future appraisals.

References

(1) R. O. McCaldin, and P. A. Kenline. *Air Pollution in Connecticut.* Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, 1957.

(2) E. R. Hendrickson, D. M. Kagy, and R. L. Stockman. *Evaluation of Air Pollution in the State of Washington.* Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, December 1956.

(3) P. A. Kenline. *Appraisal of Air Pollution in Tennessee.* Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, 1957.

(4) O. Paganini, M. D. High, and P. A. Kenline. *Appraisal of Air Pollution in Texas,* Texas State Department of Health, Austin, Texas, 1958.

Air Pollution Research Planning Seminar

February 5-7, 1958

Report of Committee on Aerosols

A seminar on "Air Pollution Research Planning" was held at the Robert A. Taft Sanitary Engineering Center in Cincinnati on February 3 to 7, 1958, under the auspices of the Public Health Service.

The non-medical portion of the seminar was divided into six separate groups for discussion. On the last day the report of each of these groups was read before a general meeting.

Your editor who attended the seminar thought that the results of the various discussions as shown in the reports, would be of interest to APCA members, and made arrangements with the Public Health Service to publish them in the Journal.

As anticipated it has proved difficult to consider the solid and liquid phases of the atmosphere apart from the gas phase and instrumentation required for measurement and analysis. In consequence, the proceedings of the Aerosol Committee may have overlapped those of other groups and the following summary report in all probability infringes, at some points, the assigned interests of some of the other Committees.

The status of knowledge of atmospheric aerosols is such that there is need for substantial research and development in almost all phases. A major shift of interest has occurred recently as the result of apparent demonstrations that aerosols, in addition to their nuisance values as primary entities, also participate in and are a part of reaction systems in polluted community atmospheres. They appear to be related closely to processes resulting in oxidations, in the formation of irritants and potential toxicants, and their intervention may influence the mechanisms and rates of photochemical processes. In addition, the visibility reduction already identified with primary aerosols, appears to be strongly fortified by the formation and growth of secondary aerosols, particularly under the influence of solar radiation.

The expansion of research activity relative to aerosols has resulted directly from the design and use of instruments and methods specifically designed to assess the more or less transient properties of particles in dynamic equilibrium with a reactive gaseous environment. Future advances in knowledge of the properties of this class of pollutants will be largely dependent on the successful development of mensuration and analytical techniques of sufficient resolving power to enable determination of spatial properties and events in a size range difficult to examine by optical means, and having a limited existence in time.

It is clearly recognized that the exigencies of various local air pollution control problems require the prompt accumulation of certain measurements, and other data applicable to identification of sources, patterns of aerial distribution, and design and evaluation of aerosol control techniques and equipment. Because of the more apparent than real dichotomy of interests among those participating, the following areas of recommended research interest are divided into two general categories. One comprises studies specifically directed toward analysis of the physicochemical system including aerosols. The second includes project areas from which needed control data can be derived with reasonable speed.

No effort has been made to establish priority of effort respecting either group.

A. Recommended research areas aimed at understanding the system to be controlled:

(1) The study of the formation, growth, and fate of aerosols.

Evidence was presented indicating that there is a close relationship between the formative process for particulates of certain types and the

development of irritative and other nuisance properties in irradiated atmospheric systems. It is further agreed that knowledge is needed of the persistence of both primary and secondary aerosols, and of the mechanisms by which they are cleared from the atmosphere.

(2) Investigations of the interaction between particles and their gaseous environments.

It was agreed that intensive studies should be directed toward determination of the dynamic equilibrium dependence of such systems on

(a) the nature of the gas
(b) the chemical species of the particle
(c) the size of the particle
(d) the temperature of the system
(e) the luminous flux
(f) the partial pressure and particle density of the system.

The conduct of work in this area will require the development or modification of instrumental techniques having a wide order of precision and capable of considerable resolution with respect to both linear dimensions and time. The concept of dynamic equilibrium implies that attention be paid to transient intermediate chemical products and states of adsorption, as well as to the build-up of terminal products. Obviously, initial efforts toward definition of the properties of aerosol gas systems should be patterned as nearly as practicable on the basis of what is already known about the content of atmospheres in communities troubled by air pollution.

(3) Investigations designed to characterize airborne particles with respect to composition, surface energy state, electrical charge, and other experimentally determinable perimeters.

In a sense, the type of information to be produced in these studies will be basic to the study of equilibrium phenomena proposed in the preceding project area.

(4) Studies of the sensitization of photochemical oxidations and other reactions at the interface between particle and gas.

Recent work has indicated that certain metallic oxides and other solid substances may intervene strongly in the types of photochemical processes which have already been described as existing over several communities. Estimates of the quantitative contribution of surface phenomena of this type to the air pollution problem requires investigation.

(5) Investigations of the relationship of aerosols and their process of formation and growth to the production of eye irritants, plant damage, and other evidences of pollution.

Strong evidence was presented before the Committee indicating that a relationship exists between the aerosol phase of a polluted atmosphere and the degree to which that atmosphere is capable of causing eye irritation after irradiation by sunlight.

B. Recommended research needs for immediate application in existing control programs:

(1) The collection and collation of available data on the size, shape, physical properties, and chemical nature of particles from identified sources of pollution.

It is believed that publication of a compendium of methods, identifying characteristics, and photographs would be of material assistance in local operations aimed at control of specific classes of source.

(2) Expansion of surveys for the establishment of patterns of variation in distribution of aerosols in relation to discrete and disperse sources.

This type of investigation is already in process in a few localities but has not yet developed to such a degree that it is possible to establish generalizations of wide applicability. These studies necessarily involve measurements of meteorological factors as well as contaminants.

(3) Development of specific measurement and analytical techniques and instrumentation.

While this field of interest was specifically assigned to the Instrumentation Committee, the Aerosol Committee wishes to emphasize the extreme importance attached to the need for adequate and relatively inexpensive devices, easily applied to field assignments.

(4) Studies of atmospheric transparency as related to aerosol content in the community atmosphere.

Probably the largest single need for adequate correlation of visibility with other atmospheric measurements is a useable inexpensive instrument for measuring light transmission and light scattering. Again, it is assumed that requirements in this connection merely reinforce the need recognized by the Instrumentation Committee.

(5) Research designed to contribute to source control of aerosols.

In particular, it is felt that additional analyses of distribution patterns from individual sources are needed; that a considerable amount of improvement can be attained with respect to the suppression and control of aerosols at the source, and that the employment of specific tracers in the analysis of distribution from primary sources should be more fully explored. Presumably, recommendations covering these needs will be made by the Committee on Engineering.

It may be apparent that no account has been taken of the problems surrounding biological aerosols or radioactive particulate matter in the atmosphere. While these two areas were discussed by the Committee, it was generally agreed that under existing conditions of distribution of interest it was not appropriate for the Committee to do more than recognize the existence of occasional problems involving these two classes of pollutants. — ***L. A. Chambers, Chairman.***

PHS Seminar Reports

Report of the Agricultural Committee

Air pollution research as its affects agriculture has had, and is receiving, considerable attention in many problem areas. However, the work in this field has not been sufficiently organized on a national basis. Special problems have received special emphasis, so that much of the work has been of a fortuitous nature. Last year's report of this committee provided a good summary of some of the major problems needing attention, and gave particular priority to fluorine effects as needing research in the immediate future. It is recognized that the greatest sparcity of information exists in the field of fundamental research; however, numerous problems still need to be solved in the applied field. It is recognized that some advances in these areas have been made during the past year.

Some modifications of that report have been suggested by this year's committee. These include *(1)* added stress on the determination and diagnosis of injuries that may result from exposure to relatively low level concentrations of pollutants over long periods, *(2)* effects of gas mixtures, *(3)* improved damage survey techniques, and *(4)* the orientation of fundamental research programs to the effects of field-encountered concentrations of major pollutants on vital plant process.

Now that some of the more obvious effects of single air contaminant compounds to certain crop plants and animals can be readily recognized, new emphasis will likely be placed on the detection of the less obvious, but still important, effects, and on injuries to economic crop plants, trees, and animals that have received scant attention in the past.

Research on the effects of air pollution upon the national agricultural economy is usually stimulated by local pressure groups concerned with a specific grievance. Although this admittedly allows the description of the problem, the motivation generally does not provide a sound basis for an interdisciplinary research effort. Investigation are, at times, initiated because funds are made available to an integrated interdisciplinary research effort. Investigations are, at times, initiated because funds are made available to an investigator already involved in a related field of study. Other programs are begun either because the effects cannot be specifically ascribed to known air contaminants or the effect of a newly recognized air contaminant is not known.

It is generally conceded that research established for the purpose of determining the effects of specific contaminants upon livestock and vegetation must be conducted under controlled or described conditions which recognize experienced toxicant concentrations, genetic composition, nutritional status, physiologic function, and external environmental factors. Programs of this kind not only satisfy the local needs for information but aid greatly in acceleration of research activity at a national level.

Exchange of ideas among air pollution research administrators is not nearly as important as it is among research workers. Common avenues of exchange include national science conclaves, specific society activities, symposia, and personal contact. The establishment of periodicals dedicated to the multidisciplinary field of research in air pollution, together with an appropriate abstracting service, will do much to foster exchange of ideas.

The Committee recommends that the U. S. Public Health Service continue to maintain liaison with private, industrial, and public research organizations. The Committee further recommends that the pioneering research laboratories of the U. S. Department of Agriculture undertake basic research on air pollution affecting plants and animals. The Committee urges that in research studies emphasis be placed on realistic levels of concentration and related environmental factors experienced under field conditions.

The need is recognized for establishment of a means for active encouragement of current publication of results of air pollution studies, for periodic critical reviews of technical publications, and for provision of authoritative information in this field. Possibilities for meeting this need should be explored.

We urge that meetings of this kind be continued and that regional symposia be held to provide for the type of information interchange needed to lead, in the near future, to a more coordinated research program on the effects of air contamination on all phases of agriculture and forestry. The air pollution program may well consider inviting administrators to attend the next meeting for discussion of research programs and exchange of ideas. Private industry, states, colleges, research institutes, and the Federal Government should all continue to feel a responsibility for parts in such a coordinated program. — ***F. E. Gartrell, Chairman.***

PHS Seminar Reports

Report of the Chemical Committee

The Chemical Committee sought to compare fields of interest of various of its members and to evaluate the current status of and future needs for, analytical methods pertaining to the identification and estimation of air pollutants. The committee discussed various areas of interest that were considered to be of special importance and considered possible approaches for the solution of the assorted problems.

The scope of the deliberations was restricted essentially to analytical problems. The matter of atmospheric chemistry was discussed briefly, and considerable and general interest was shown in this topic. The consensus was that, while this area fell within the province of the Chemical Committee, time did not permit a detailed presentation of the current status or the possible development of this subject.

Techniques

Various broad developments were discussed in regard to current applications in air pollution work. Certain *new* techniques were considered from the standpoint of possible development as tools for air pollution studies.

Sampling

Sampling was considered to be one of the most important areas for consideration. It is believed that both adsorption and condensation techniques justify more detailed study and comparison. With the rapidly expanding interest in organic air pollutants, freeze-out methods, and adsorption on activated charcoal and similar materials, has become critically important. Both approaches have been widely used in the past, but in many applications the amounts of sample available were such that the stringent limitations of air pollution were not met.

Grab samples are caught in many ways. Bags of polyethylene, rubber, Saran, and similar synthetic sheeting have different adsorptive characteristics and retention abilities. Careful study should be made of the suitability of such materials for the collection of various types of pollutants.

Scrubbers of various types have been developed but critical studies are still needed to establish the effectiveness of such scrubbers under various conditions of flow rate, temperature, and concentration. It is highly desirable that absorption liquids selectively extract pollutants and, where possible, so stabilize the collected material that changes in composition are minimized even when prolonged standing may be necessary. The desirability of simultaneous isolation and measurement was recognized and hope was expressed that more methods could be developed where collection and measurement would preclude errors due to loss or chemical change.

Gas Liquid Chromatography

This tool presents one of the brightest hopes in the study of air pollution problems. It solves problems in both the separation and the analysis of pollutants. The cost of equipment is relatively low, and the techniques are sufficiently simple that it is reasonable to expect that present personnel in most laboratories can apply the technique when suitable methods are developed. Absolute identification of compounds cannot be made with this approach, but the availability of catalogs of retention times for various standardized colums will make gas liquid chromatography very useful for air pollution surveys. Where individual compounds are sought, the identity and concentration can often be established by this approach. Where complex atmospheres are sampled, chromatographic separation of components can assist greatly in facilitating subsequent analyses by infrared, mass spectrographic, polarographic, and chemical techniques.

Infrared

Long path infrared techniques have proved invaluable in extending our knowledge of air pollutants. In spite of its cost and the fact that it requires skilled technicians for its proper exploitation, it remains probably as the most valuable means of studying dynamic systems. It presents a panoramic picture of transitory and exotic substances that might go completely unnoticed where more conventional techniques are applied.

Ring Oven

The ring oven technique recently developed by Weisz was proposed for application in conventional separations of minute amounts of material. Although little work has been done on its application in the air pollution field, it does hold considerable promise in the separation, characterization, and identification of air pollutants. It is particularly promising for studies of collected dusts. (*cf. Stephen, W. I., Research, 10, 429-436 (1957)*).

Mass Spectrometry

Mass spectrometry is established as a useful tool in the development of air pollution analytical methods. At present its major promise is in the identification of materials isolated by chromatographic, sublimination and extractive procedures. Applications have been made to the characterization of freeze-out samples.

Polarography and Anodic Stripping Voltammetry

Polarographic methods have found application in the study of both organic and inorganic pollutants. The sensitivity obtained is sufficient for many studies and both quantitative and limited qualitative applications are indicated. Anodic stripping voltammetry possesses exceptional sensitivity and might very well be investigated for possible use in the determination of extremely small traces of various metals.

Microwave Spectrometry and Related Techniques

These methods are recognized as important laboratory research tools.

Their direct application to air pollution problems seems very limited at this time.

Dust Identification

In addition to fine particle identification by means of optical characterizations (polarized light) recognition is given to the potential value of a systematic compendium of the morphological characteristics of a wide variety of inorganic and organic dusts.

Biological Methods

Plant damage, cellular and enzymatic studies provide valuable information. Such methods hold considerable promise of development for both general and specific determinations of pollutants.

Miscellaneous Techniques

Electron microscopy, X-ray spectrometry, X-ray diffraction, X-ray fluorescence, and related techniques find specific applications in air pollution studies and further developments are anticipated.

Special Problems

Probably no methods of sampling, detection or estimation can be considered so perfect that further development is unlikely. Certain known or suspected pollutants of importance justify more immediate emphasis.

Nitroolefins and other organic nitrogen compounds, peroxides, organohalogens, boron compounds, ozone, fluorides, organophosphorus compounds, organic sulfides and mercaptans, carcinogenic substances, and oxides of nitrogen all are of great current interest and justify detailed study from the standpoint of the development of appropriate analytical methods, and the application of such methods to field and laboratory studies.

An analytical method for obtaining some sort of index of pollution is badly needed. Such an index would be non-specific and arbitrary, but might nevertheless be useful to the extent that it could be correlated with observed effects. One possible approach might be to measure solid, liquid and absorbed gaseous pollutants in terms of beat frequency change of a high frequency oscillator. Another approach might be to correlate total weight of particulate matter together with gas conductivity measurements on intermittently sorbed and desorbed gaseous materials. Measurement of decay rates, whether of ionized or merely chemically labile species, might serve as a useful index.

Conclusion

Further progress in understanding polluted atmospheres is entirely dependent on improved analytical methods. These will require the expenditure of time and funds; however, these must be expended if clear answers are to be obtained.—***Philip W. West, Chairman.***

PHS Seminar Reports

Report of the Engineering Committee

The deliberations of the Committee have been concerned with the various aspects of the air pollution problem involving engineering, including the evaluation of the need for and the extent of control measures, and the economic applications of indicated control measures either at the source or in the field. The Committee feels that the rate of progress in the engineering aspects of air pollution has been entirely inadequate in the light of the economic importance of the problem. Current total research expenditures are estimated to be on the order of 0.1% of the total economic burden of air pollution to the nation. In addition to the relatively low research expenditure, a large portion of these expenditures fall into what may be termed *engineering application* rather than actual research.

It is, therefore, the considered opinion of the Committee that future research activities lean more heavily to the basic side than has been the case. With this in mind, the recommendations have been expressed in broad categories rather than for specific important isolated items.

This Committee wishes to reiterate the conclusion drawn at the last Air Pollution Research Planning Seminar that control at the source by process design or modification is a most desirable approach. It is recognized, however, that in many cases effective control by this means may not be generally economically feasible. Because of the wide variety of such problems and because of the many intangibles that have to be considered in such decisions, the Committee feels that this area is not a fruitful area for general research. This is not intended to preclude the desirability of doing such research in specific instances nor to reflect on the desirability of emphasizing this aspect in design considerations.

The recommendations on the following pages summarize the conclusions of the Committee.

Characteristics and Quantity of Atmospheric Contaminants

A. The Committee believes that there is an urgent need for a compendium of the nature and amounts of specific atmospheric contaminants. Such a compendium, in conjunction with other data on the effects of specific contaminants, would provide *(1)* a basis for assessing the air pollution potential of a specific city or area, *(2)* a basis for assessing the relative need for control measures for specific contaminants in the area, and *(3)* a basis for formulating or revising specific air pollution regulation for the area. While compendia of this type have been obtained in specific instances, it is the intent to en-

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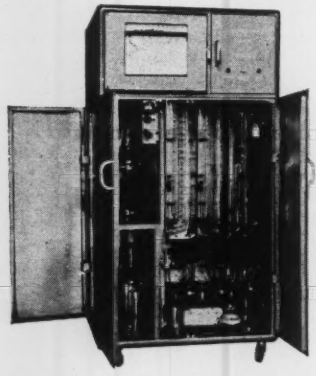

CHEMICAL TYPE
for measuring:
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NITROGEN DIOXIDE
NITRIC OXIDE
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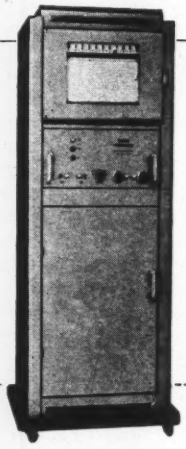
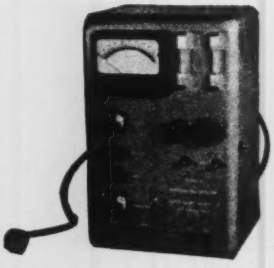
Max. sensitivity: 0.8 ppm full scale



ULTRAVIOLET PHOTOMETER
for measuring:
OZONE
VISIBILITY
Max. sensitivity: 1 ppm full scale



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for measuring:
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large and generalize such information. The first step would provide a classification by operation, process, and industry. Further analysis and correlation might provide useful information on the bases of broader classifications such as geographical area, industrial concentration, *etc.* To enhance potential application, attempts should be made to correlate these data on such bases as quantity of contaminant per capital, per dollar sales, per employee, etc. Such correlations, in essence, represent an attempt to arrive at techniques analogous to those used in market surveys.

B. There is an urgent need for fundamental bases for extending information on quantity of emission of a contaminant, or its precursor, to actual field manifestations. The first step in such a relationship requires the development of basic information on the deposition and retention of particulates, gases, and vapors on surfaces of all kinds, such as walls, ground, vegetation, *etc.* The subsequent effects of such retained deposits are in the domain of other committees concerned with specific areas of effect, such as agricultural damage.

Results of such an investigation would also be applicable in the area of remedial equipment performance, in which area some work on deposition has already been carried out. There has been substantially no work along the lines of retentivity.

C. It has been customary to characterize particulates by size. The Committee wishes to emphasize that particle size is rarely measured directly. Some other characteristic of the particle is measured which is then interpreted in terms of an effective size by means of some theoretical or empirical relationship. In considering the behavior of a particle in some apparatus or process, it is, therefore, essential that the method of measurement used to obtain the effective particle size involve a measure of the same characteristic of the particle which determines its behavior in the process. For example, in defining the performance of inertial separating devices, it is the particle inertia which is of prime importance. The effective size of such a particle should then be based on a measurement involving particle inertia, such as settling velocity. In other devices, such as cloth collectors, other characteristics, not yet clearly defined, are of prime importance. It is desirable, therefore, to develop the basis to be used for particle size specification in a variety

of operations. The question of characterizing a particle in terms of effective particle size is merely a matter of semantics. It is essential, however, that the inherent characteristic described by this effective size be clearly kept in mind in relation to the operation under consideration.

It has also been widespread practice to measure particle size in terms of the size of the discrete particles. In an air stream the particles are not necessarily present as discrete particles but are flocculated to a greater or lesser extent, depending on previous history. The behavior of the particles will be determined by the characteristics, not of the individual particles, but of the flocs. It is essential, therefore, that a measurement aimed at characterizing such particles in gas suspension measure the characteristic property of the flocs as they exist in the gas stream and not the characteristic property of the discrete particles. Failure to consider this factor may often introduce a major fallacy.

Thus the *effective* particle size as used hereinafter will refer to a size based on a measurement of characteristic property of particles (flocs) as they exist in suspension, the specific characteristic property being determined by the application under consideration.

D. Principles of particle behavior have been determined largely for atmospheric temperature conditions. While, in some cases, theoretical bases exist for applying the principles to high temperatures, other factors may enter or become controlling. With the current importance of high temperature operations, it is important, therefore, that experimental and theoretical investigation be undertaken to establish principles of particle behavior at elevated temperatures.

Evaluation Techniques

A. The Committee feels that progress in the application of engineering to air pollution control of particulates is most seriously limited by the current inadequacy or lack of two basic tools:

(1) A means for reproducibly generating both solid and liquid test aerosols, of relatively homogeneous size, and relatively complete dispersion in a range of size from, say, 0.1 to 10 μ, and with a variety of materials and shapes. While several techniques

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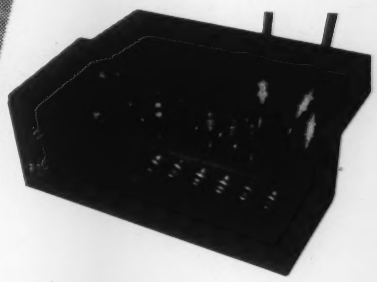

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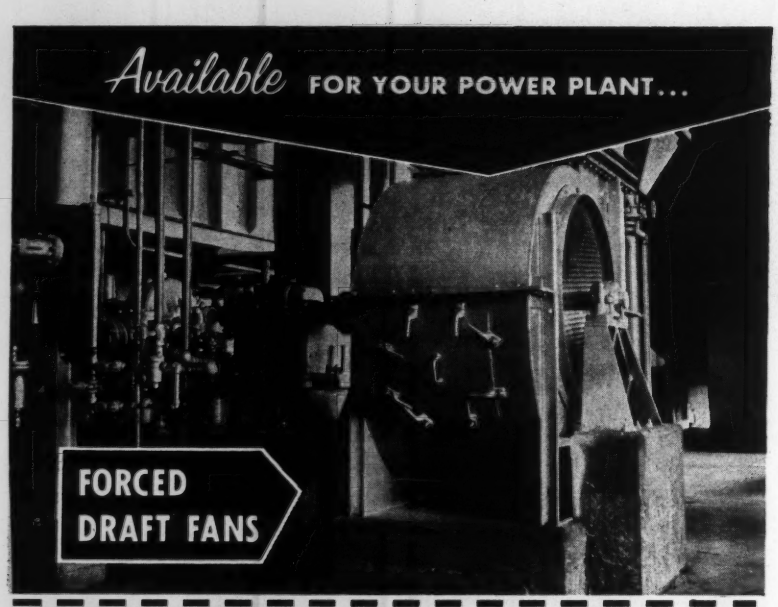

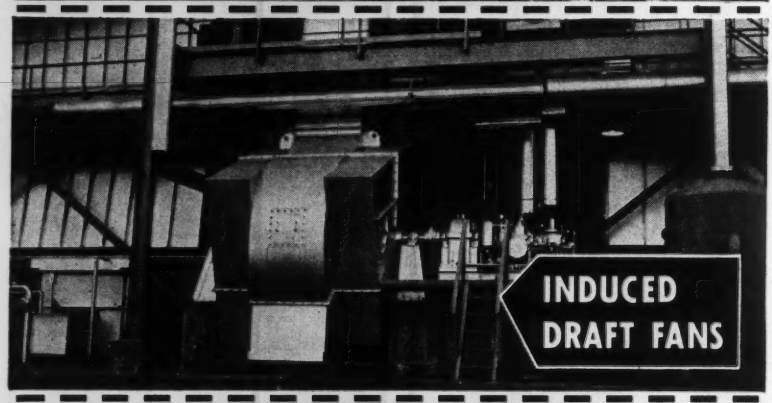

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are currently available for this purpose, they all involve serious limitations either in quantity of aerosol produced, flexibility, or control.

(2) Means for measuring *effective* particle size, as defined above, for a variety of pertinent characteristic properties, and applicable for measurements of size of particles as they exist in suspension.

The Committee strongly recommends that development in these two areas receive high priority on both short term and long term bases.

B. In the evaluation of particulate control equipment, the use of so-called "standard" test dusts has received great prominence. This has been a necessity because of a lack of better means of evaluation. Because of the inherent limitations and the relative futility of past evaluations by this means, the Committee feels that, except for special areas of application, the emphasis on development of such dusts be minimized in favor of a greater emphasis on generation of homogeneous aerosols as discussed above. The Committee recognizes that, in the interim, *standard* test dusts will still find a role in current equipment evaluation.

C. One serious drawback to the further progress of control of gaseous contaminants is the limitation imposed by subjective measurements. It is, therefore, suggested that consideration be given to further development and refinement of subjective measurements of gaseous contaminants such as eye irritants and odors. It is believed desirable to investigate the feasibility of physical and chemical methods related to subjective methods with a view to supplementing these methods. The development of these techniques may logically fall within the scope of disciplines other than engineering.

Control Measures

It is felt that sufficient importance has not been attached to the air pollution problem in the process development and plant design phase. We, therefore, recommend that an effort be made to make engineers sufficiently aware of the air pollution problem so that it will receive adequate consideration in design.

A. While there has been considerable evaluation of the performance of remedial equipment in specific applications, there is an extensive need for

information which is both more definitive of comparative performance characteristics and more generally applicable to a variety of problems The Committee suggests, therefore, that evaluation of remedial equipment performance be conducted at a more basic level than has been the case, utilizing where available and applicable, techniques of the types suggested in the previous section. It is not uncommon, and may be desirable, to carry along technique developments and equipment evaluation simultaneously. The above mentioned evaluation should be aimed at developing sound selection and design criteria for remedial equipment installation.

B. The Committee recognizes that work is in progress in development of remedial measures for removal of contaminants from combustion and pyrometallurgical process exhausts, such as the internal combustion engines, steam-generating facilities, metallurgical furnaces, incinerators, *etc.* The Committee believes, however, that accelerated research is indicated, aimed not only toward the development of adequate equipment but also to a more thorough economic comparison of alternative equipment. Such research must consider not only the mechanical operability at elevated temperatures but any unique factors introduced by the elevated temperature on performance characteristics.

C. The Committee recommends that evaluations be made to determine the feasibility of fuel modifications for the removal of specific components which contribute to the formation of noxious gaseous contaminants. — ***C. E. Lapple, Chairman.***

PHS Seminar Reports

Report of the Instrumentation Committee

The Committee chose as its framework the development of two types of information in three areas;

(1) Atmospheric Analyses

(2) Source Analyses

(3) Laboratory Research

namely, the state of the art and the needs for additional research and development.

Atmospheric Analyses — Gas Phase

The state of the art in this field is quite advanced in that one can draw on a large variety of recording colorimeters and spectrometers for such pollutants as oxidant, ozone nitric oxide, nitrogen dioxide, carbon monoxide and sulfur dioxide. Certain recording conductivity instruments are available for certain applications.

The outstanding need in this area is an instrument which is portable (25-50 lb.) and less than $500 each. The directions one might look for such a development are:

(1) The use of spot tests wherein the reagents are imbedded in the filter medium through which the sample gas will pass. Colorimetric standards would be developed for each gas to be analyzed.

(2) The use of physical properties of gases for their identification and concentration measurement such as absorption spectrometry with simple filter photometers.

Secondary needs are component developments for existing colorimeters and spectrometers such as a liquid pump for the stable discharge of small quantities circa 1 ml./min.; development of gas chromatographic techniques for direct analyses in the ppm. range; and the development of special mass spectrometers.

Finally the need for two specific instruments was suggested, namely an ethylene recorder and a total combined nitrogen device.

Atmospheric Analyses—Aerosol Phase

The state of the art in characterizing the physical characteristics such as number density and size distribution is exemplified by three types of instruments; the cascade impactor and the corollary use of optical and electron microscopes, the electronic light scattering photometer counter and Goetz particle spectrometer. The recent development of the Cahn microbalance (portable and rapid) brings the microgram weighing problem well in hand. One still needs method for measuring index of refraction for the submicron particles.

There is now a fair variety of sampling apparatus. There is a need for *(1)* filter media with satisfactory chemical and physical properties for spectrographic, gravimetric and chemical analyses; *(2)* high volume delivery pump with a fixed flow rate against a variable head; and *(3)* very high volume filter techniques for collection of large samples for the accurate measurement of materials in very low concentrations.

In the interest of making more economical large survey there is a need for spot tests for particulate matter using reagents in the filter medium.

Atmospheric Analyses—Meteorology

In a joint meeting with the Meteorology group it was agreed that the latter would present their findings in their report. We developed separately and then concurred on the need for visibility instrumentation and this need might be met most easily by evaluating the following developments and standardizing on the best:

(1) Sinclair Phoenix

(2) Chaney Visibility Meter

(3) Duntly Meteorological Range

(4) High sensitivity Photometer

(5) O'Konski 90° light scattering Photometer

We developed separately and then concurred on the need for a rugged reliable wind velocity and direction recorder for less than $300.

Atmospheric Analyses—Data Processing

The state of the art of components for systems needed in this area is quite high. However, the application

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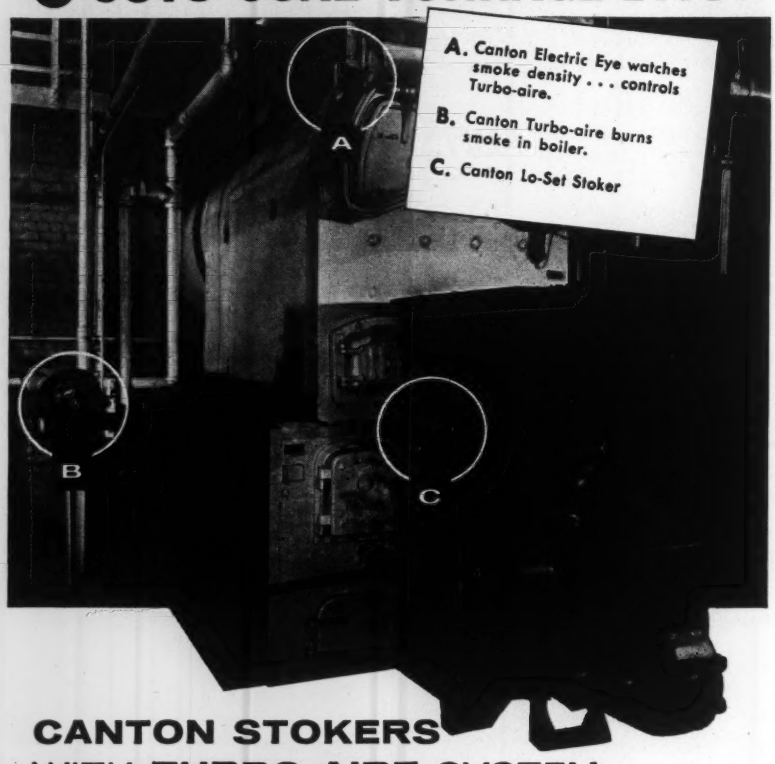
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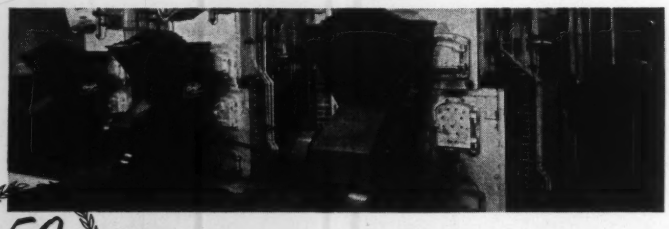

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to air pollution measurements has been slow and much work remains to be done. In particular one must go back to the data gathering instrument designs to incorporate devices for the ready translation of the data to manipulation and analysis processes. This principle applies across the board to chemical, physical, and meteorological measurements.

Source Analyses—Gas Phase

The state of art in this area is exemplified by such devices as the carbon monoxide, carbon dioxide, and total hydrocarbon infrared recorder, nitric oxide and sulfur dioxide infrared recorders, nitrogen dioxide ultraviolet recorders. The needs are *(1)* the measurement of the total organics from industrial operations such as these involving solvent emissions *(2)* the development of gas chromotographic techniques to cover the oxygenated hydrocarbons and the higher hydrocarbons, say up to C_{10}.

Source Analyses—Aerosol

The state of the art in this area is low from the point of view of automatic continuous instrumentation. The outstanding need is for an objective method for plume evaluation. However, there is also a need for sensing continuously the weight or mass emissions from stacks. The plume problem might be evaluated on the basis of count of the such micron particles (.2 to 1 μ diam.). One would have to develop a portable particle counter to fill this need. However, one may also be faced with the same problem of counting particles even smaller than .2 μ because after leaving the stack they may grow or coagulate and thus enter the .2 to 1 μ range due to physical and/or chemical processes in the atmosphere.

One may fill this need with recording condensation nuclei meters or possibly an instrument based on the principle of the shift in polarization of light phenomena involved in the scattering process.

Laboratory Research—Gas Phase

The state of the art in studying the chemistry of photochemical reactions at high dilutions is quite advanced due to work of the Franklin Institute with long path infrared spectroscopy. The earlier work of Haagen-Smit, the Los Angeles Air Pollution Control District, and the Stanford Research Institute were vital

links in the chain of events that led to the present status. It appears that the recent rapid development and application of gas chromatography to this field will even further our knowledge of this chemistry. The need now is to extend the usefulness of infrared and mass spectrometry, particularly in sensitivity, so that they are able to analyze the components of the mixtures so well separated by the gas chromatographic systems.

It was suggested that one other instrument system might contribute to the elucidation of the chemistry namely long path ultraviolet spectrometry. Finally we call attention to two other techniques which may be called upon, namely *(1)* NMR for hydrogen and nitrogen bonding in complex molecules and *(2)* EPR for free radical species.

Laboratory Research—Aerosol

The state of the art in this area has been well advanced by the work of three schools: La Mer *et al.* at Columbia, Gucker O'Konski *et al.* at Indiana, and Berkeley and Goetz at Cal Tech. The outstanding need appears to be that concerned with the chemical nature of adsorbed layers on the particulate. There are, of course, also some difficult problems with identifying the substrate mentioned under the section atmosphere analyses—aerosol. It was suggested that infrared spectrometry might be applied to the analysis for organic compounds in the adsorbed layer. In the study of number density and size distribution below .2 μ diam. there is a need to extend the lower limits of the light scattering and centrifuge devices. — ***N. A. Renzetti, Chairman.***

PHS Seminar Reports

Report of the Meteorology Committee

The Meteorology Panel has purposely focused attention on one fundamental aspect of the community air pollution problem—that of quantitative specifications of atmospheric dispersal capacity. It is recognized that ultimate solution of the problem depends upon a satisfactory understanding of many other aspects all of which have important bearing on air pollution. These factors have been well enumerated in the report of the first Meteorology Panel which has been used as a point of departure for this year's deliberations.

From the planning standpoint, the Panel recognizes three categories of meteorological research which will tend to advance the control of community air pollution:

Category 1. Direct participation by meteorologists in specific community pollution studies.

Research in this category is inherently not susceptible to planning by a Panel of this sort. The needs will be determined by the peculiar problems of the individual community. The Panel notes, however, that the consultant or participating meteorologist can draw upon a considerable fund of existing knowledge and experience in developing a research plan to meet the objectives of the study. In particular, the meteorologist should be prepared to provide general assistance on such problems as:

(a) The comparison of atmospheric *dilution potential* or *ventilation* at different geographical locations by means of indices based on available climatological data.

(b) Formulation of zoning or city planning criteria for the location of certain types in industry with respect to residential areas.

(c) Determination, for regulatory purposes, of limiting rates of pollutant emission from industrial plants or complexes.

(d) Identification and location of unknown sources of observed pollution.

(e) Design of air pollution sampling programs.

(f) Identification and prediction of meteorological conditions leading to severe air pollution episodes.

Category 2. Meterological research aimed at providing information directly applicable to the problem of community air pollution.

This category does lend itself to coordinated planning, and the specific recommendations of the Panel are detailed in later sections of this report.

Category 3. Basic research.

Independent, relatively small-scale research efforts in areas such as atmospheric turbulence and diffusion, microclimatology, aerosol physics, atmospheric chemistry and meteorological measurement problems can be expected in the long run to improve the scientific basis for the more immediately practical studies mentioned above. The planning of research in this category is the prerogative of the investigator. While the Panel deplores the inadequacy of support now available for such independent basic research, we are hopeful that discussions presently underway at high levels of government will soon lead to an improvement.

Complete information on past investigations is a natural starting point in the consideration of any future community air pollution research program. The committee understands that a large body of basic atmospheric dispersion data exists but is not generally available because of agency security classification levels.

The committee strongly urges that government agencies possessing such atmospheric dispersion data review the reports of their own research and those of their contractors with the object of declassifying and making generally available all pertinent dispersion and related meteorological data except that which may be absolutely essential to the national security. We feel confident that much of the available material could be released in a form that would adequately convey the essential physical information without compromising security.

The committee is convinced that the release and distribution of pertinent classified diffusion material is

essential to the most efficient and economical development of a community air pollution program. We feel that the responsibility for releasing and disseminating this material should be assigned to an individual or a small committee having sufficient authority to proceed.

Recommended experimental attack on intermediate-scale diffusion

The panel is convinced that the time is ripe for a major experimental attack on the problem of atmospheric transport and dispersal on the scale of a large metropolitan area. We are convinced that little further progress can be made in quantative understanding of urban pollution without such an organized program. We are convinced that the means for the successful execution of such a program are at hand.

Satisfactory quantitative estimates of the capacity of the atmosphere for transporting and dispersing airborne contaminants are requisite for an objective evaluation of the community air pollution problem and, in particular, for the framing of effective regulatory measures. The fundamental scientific problem is that of establishing suitable relationships between dispersive capacity and meteorological parameters that serve as direct indicators of turbulent mixing. These relationships may then be used to predict the three-dimensional distribution of airborne material, under a wide variety of weather conditions, emitted from sources of known characteristics.

Comprehensive, accurate measurements of dispersal and appropriate meteorological parameters are almost entirely lacking for the intermediate—and large-scale processes responsible for community air pollution. The research program described below is primarily intended to provide basic information on the physical processes by which the atmosphere disperses airborne contaminants.

(1) Scale of the experiments—0 to 50 miles.

(2) Sites — The initial site should be a typical city in relatively flat terrain in the mid-western U. S., free of obviously unique meteorological characteristics. A second, and perhaps a third, site will be selected on the basis of increasing complexity of terrain. In each

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case the urban area should be large in relation to the 50-mile scale.

(3) The Experimental Program —This research program involves comprehensive simultaneous measurements of atmospheric transport and diffusion of materials from point sources and measurements of meteorological quantities which are related to these phenomena. These include:

(a) Determination of the three-dimensional distribution of a tracer effluent discharged from continuous point sources of known characteristics at various elevations (25-100 m.).

(b) Meteorological variables to be measured include vertical profiles of mean wind speeds and air temperatures, and the intensities and scales of turbulence at distances and heights commensurate with the spread of the tracer plume(s). Auxiliary meteorological measurements will include such parameters as solar radiation, soil temperatures and humidity. Appropriate synoptic data are a basic requirement in order to relate the results to routine meteorological measurements.

(c) The overall time scale of the experimental program at a given site is approximately 3 years, with the first year devoted to planning and preparation. An additional year at least would be required for comprehensive analysis of observational data. The subsequent tests at additional sites presumably will require shorter periods.

(d) The scope of the program is such that attention must be given to rapid data processing and analysis. The observations must be converted to a form which permits early utilization by all interested parties.

Although it is recognized that diffusion plays a major role in the dispersion of atmospheric pollutants,

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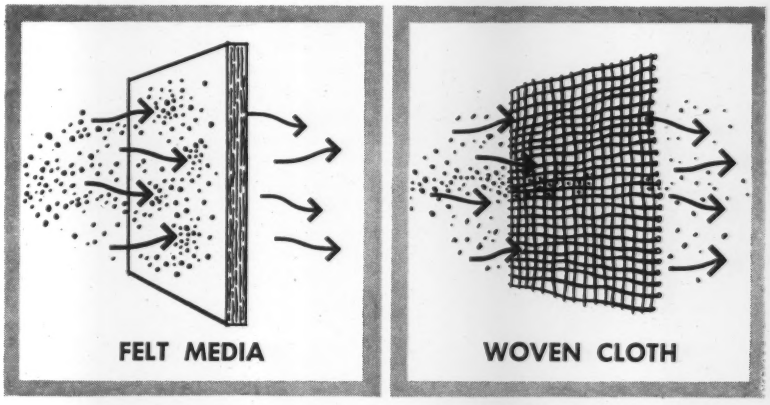

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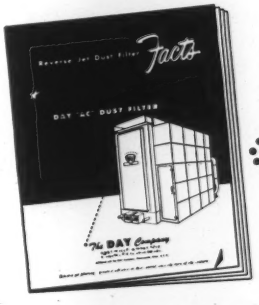

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non-diffusive processes *viz.* deposition and wind erosion, cannot be overlooked in a realistic approach to the community air pollution problem. This becomes evident when one considers the corrosive properties of many industrial dust deposits, their detrimental effects on plant life, their nuisance value, and, in the case of radioactive substances, their potential danger to health. Of the non-diffusive processes, *deposition* purifies the air, but pollutes the surface as well as animate and inanimate objects on it; in case of radioactive dusts, deposition brings the radiation closer to all living organisms. The following processes of deposition must be considered: fallout, impaction, washout, and rainout. On the other hand, wind erosion reintroduces into the air pollutants previously removed from it. For study of the above processes, tracer material of a larger size (perhaps 10 μ or larger) than that used in the study of diffusion should be employed.

Meteorological instrumentation

The recommendations given above for an extensive program of field experimentation suggest a review of meteorological techniques and instruments. In this section are summarized the deliberations of a subcommittee composed of representatives from the Instrumentation and Meteorology Panels.

There are essentially two classes of instruments pertinent to community air pollution problems, the first involving devices suitable for basic research investigations, and the second, relatively simple and inexpensive devices for routine meteorological measurements.

Research devices and techniques

Examination of the existing meteorological research equipment for community field investigations suggests that available instrumentation for ground-level measurements is generally satisfactory. There are exceptions, however, particularly:

(1) Visibility and humidity. Instruments for both of these parameters are judged inferior to most meteorological equipment in accuracy and durability.

(2) Low-velocity winds. An all-weather instrument suitable for the continuous recording of wind speed and direction in the range 0.5 to 30 mph. and yet capable of withstanding 60 mph. is not commercially available.

(3) Wind turbulence. An instrument for the measurement of wind speed and direction fluctuations in the same range, and possibly combined with *(2)*, is needed.

The development of instrumentation for measurements in the range from 100 to 5000 ft. above ground is an important field of endeavor. There is a need for measurements of turbulence, wind speed and direction, trajectories, lapse rate, humidity and visibility. Broadly speaking, the equipment is less accurate and reliable than that available for use at low levels. In some cases, it does not exist.

The committee strongly recommends that attention be devoted to tracer techniques involving either a gas or particulate matter as a basic component of research meteorological equipment. While it is difficult to establish complete specifications for such a technique in a general seminar, certain requirements can be defined:

(1) Conservation. The tracer must remain unaltered in its physical and chemical properties over appropriate sampling times and travel distances.

(2) Accuracy. The technique should provide measurements accurate to $\pm$ 10% over a concentration range of at least 3 and preferably 4 orders of magnitude.

(3) Simplicity and speed. Both collection and analysis must be rapid and reasonably simple.

(4) Emission. The rate of effluent release must be readily controllable; in the case of particulate tracers, size distribution must also be controlled.

(5) Toxicity. The tracer must be non-toxic at the concentrations used, and preferably odorless and tasteless.

(6) Visibility. An invisible tracer will be most valuable in community studies.

(7) Cost. Because of the relatively large numbers of

samples, the cost must be kept as low as possible.

Instruments for routine measurements

There are very few instruments available which meet the specifications of simplicity, durability, and low cost and yet provide the required information.

While it is beyond the scope of this seminar to establish firm recommendations for such instruments, it is considered both desirable and possible to provide this in the near future. The specifications should stress only the key functions of each device, allowing relaxation of quality in nonessential features. It is believed that the most needed instruments are those for the measurement of low-level winds and lapse rates.

Automation

Implicit in all of the above discussions is a heightened interest in time- and labor-saving devices. The tremendous number of observations demands careful consideration of the possibility of utilizing telemetering, automatic recording, standardization and computer techniques.

The role of models in air pollution studies

The use of models to reveal the relations between meteorological parameters and the diffuse capacity of the atmosphere is attractive. However, our knowledge of techniques is inadequate for this purpose. At the present time models are useful in air pollution study only for investigating special small-scale phenomena such as the air flow a mile or two downwind from an industrial complex, and optimum stack parameters. It appears that much arduous and imaginative work will be required before satisfactory meteorological modeling techniques are developed.

During the next few years the demands for information on the diffusive capacity of the atmosphere necessary to provide safeguards against potential air pollution hazards will probably increase. An extremely large expenditure will be required if field experiments must be conducted in every community to obtain the necessary information. Success in developing modeling techniques adequate to provide only a part of this information would result in a very considerable saving in time and money. Therefore, well-conceived efforts directed at the development of techniques for modeling meteorological processes related to the air pollution problem are to be encouraged.—***Thomas F. Malone, Chairman.***

Classified

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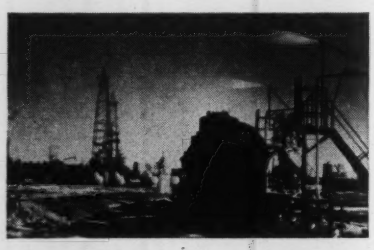
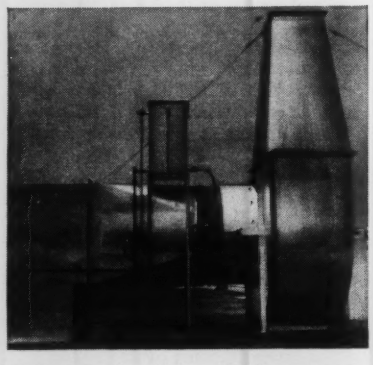
They used guns to kill odors

some interesting examples of Airkem installations

Spray guns are frequently used to vaporize Airkem odor control products for industrial application. Airkem has developed special formulas that are individually matched to the hundreds of different odor problems in industry. Here are some of the unusual examples of odor problems treated by the Airkem odor specialists.



Mercaptans, highly odorous products, are mixed in natural and manufactured gases by utility companies as a warning agent against leakage. In concentrated form they are almost unbelievably foul. A spray gun installed above the tank car vaporizes an Airkem odor control product at the loading station of a mercaptans manufacturer. Utility companies use the same product to control odors from leakage or spillage of mercaptans in their plants.



Sludge Drying has enabled many communities to convert sewage into an asset. Many plants have even made profits selling the dried sludge for fertilizer. However, the odor from the operation is not pleasant. To eliminate the odor problem in this installation, an Airkem spray unit was placed directly in the steel ducting that discharged the odorous air into the atmosphere. Equipment and controls are simple, easy to install and service.

Chemical Plants, such as this midwest ammonium sulphate installation, often create odors that disturb their neighbors. Management tried several techniques before learning about Airkem's effective and economical method. A plant employee is shown adjusting the spray gun for proper odor control.

Cement Plants have odor problems, too. Here is a New York State plant of a major cement company that uses an Airkem installation with excellent results. The odors, which smelled very much like hydrogen sulphide, caused a serious community relations problem when the wind carried them into the residential areas. The Airkem guns, installed at the top of the stack, quickly brought the odors under control.

Food Processing odors, like those released by this spaghetti sauce plant, are obnoxious to many communities. Normally zoning restrictions would have prevented this plant from operating in its present location. However, a small compressor-powered Airkem system solved the problem to the complete satisfaction of the neighborhood. Fish processors and many other food plants have also learned to rely on Airkem for effective odor control.

Odor Control Tests are continuous at Airkem's laboratory, the largest in the world devoted solely to odor studies. Here an Airkem engineer checks operation of a spray unit in the test room. Many types of evaporation equipment are used besides spray guns. There are hundreds of different formulas used by Airkem for their odor control work. Each odor is treated as a special problem, thus assuring a maximum effectiveness with minimum possible cost.

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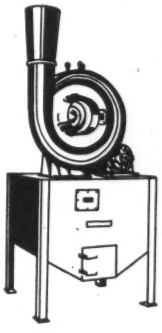

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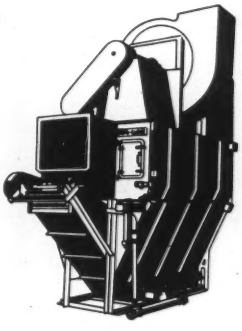

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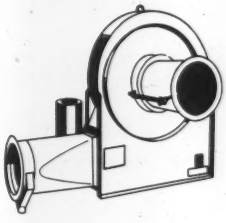

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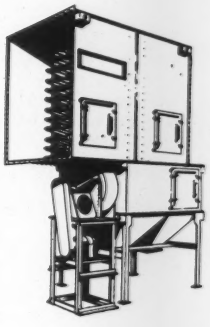

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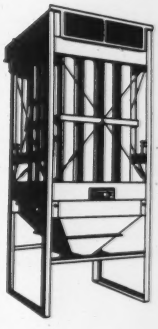

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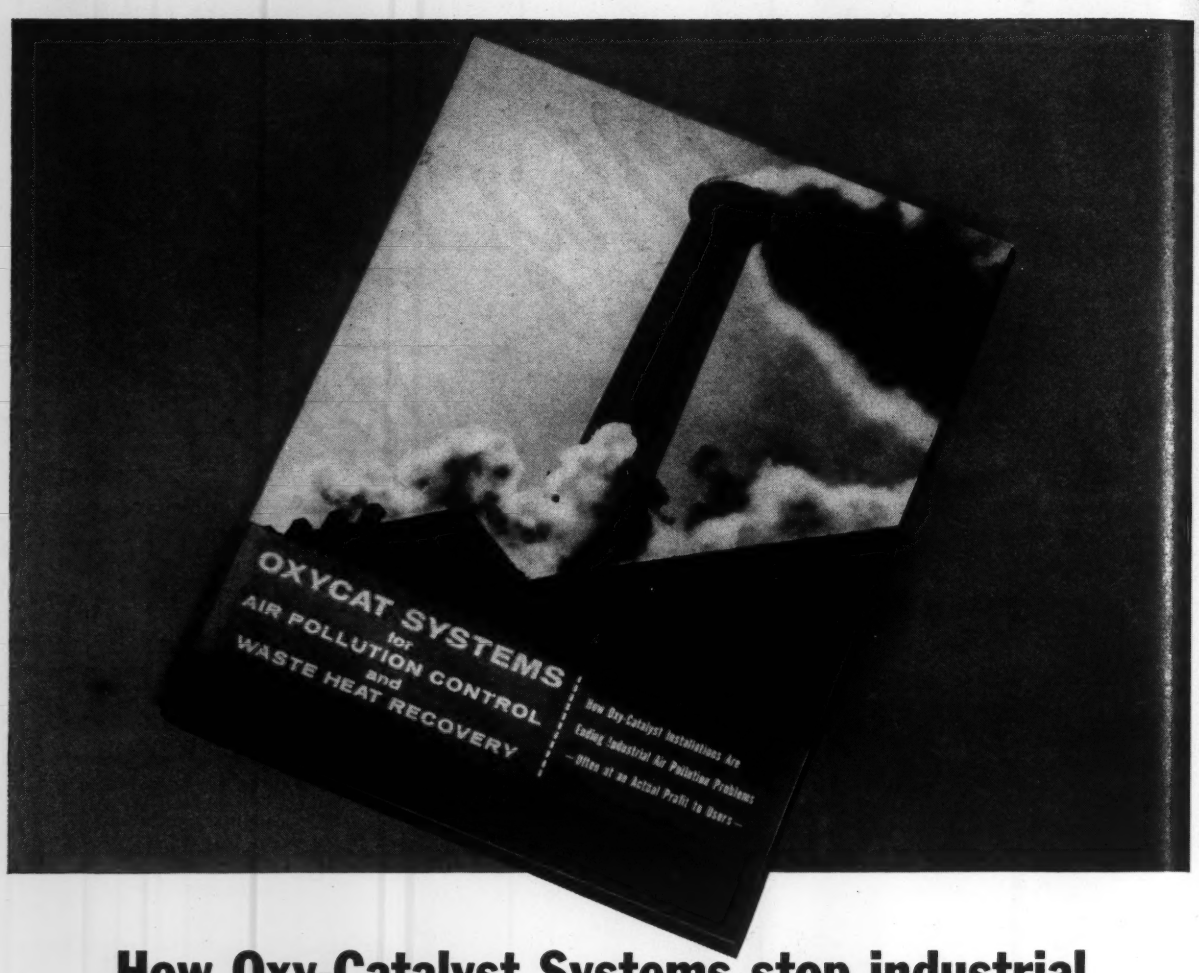

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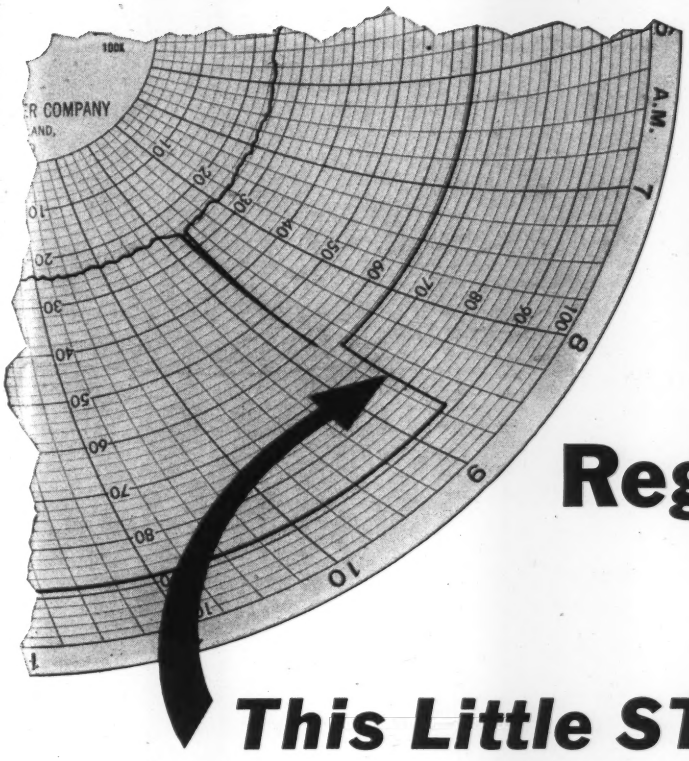

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